United States Court of Appeals

for the Second Circuit

APPENDIX

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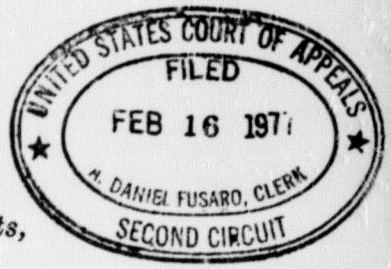
United States Court of Appeals
For the Second Circuit



EUTECTIC CORPORATION, NEW METALS CORPORATION and METALLIZING COMPANY OF AMERICA, INC.,

Plaintiffs-Appellees and Cross-Appellants,

v.

METCO, INC.,

Defendant-Appellant and Cross-Appellee.

JOINT APPENDIX

VOLUME VII OF EIGHT VOLUMES

(EXHIBITS — Pages E599 to E945)

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TABLE OF CONTENTS

PAGE

Volume I

Relevant Docket Entries ..... JA 1

Declaratory Judgment Complaint ..... JA 2

Amended Declaratory Judgment Complaint ..... JA 6

Answer and Counterclaim ..... JA 10

Reply to Counterclaim ..... JA 13

Memorandum of Decision ..... JA 16

Judgment ..... JA 101

Notice of Appeal ..... JA 103

Cross Notice of Appeal ..... JA 104

Stipulation Under Rule 29(2) Concerning Miscellaneous Discovery Information ..... JA 105

Notice of Inter Partes Testing ..... JA 107

Volume II

PAGE

EXCERPTS FROM TESTIMONY

Nicholas J. Grant:
- Direct ..... JA 110
- Cross ..... JA 218
- Redirect ..... JA 404
- Recross ..... JA 425

Louis M. Osika:
- Direct ..... JA 428
- Cross ..... JA 436
- Redirect ..... JA 438

Volume III

Mahesh S. Pastel:
- Direct ..... JA 439
- Cross ..... JA 459
- Redirect ..... JA 491
- Recross ..... JA 496

Joseph F. Quaas:
- Direct ..... JA 498
- Cross ..... JA 504

Ferdinand J. Dittrich:
- Direct ..... JA 521, JA 615
- Cross ..... JA 610, JA 637

Gary Montgomery:
- Direct ..... JA 639
- Cross ..... JA 664

Rea Axline:
- Direct ..... JA 668
- Cross ..... JA 684

Volume IV

PAGE

Benjamin Post:
Direct ..... JA 691, JA 1093
Cross ..... JA 720, JA 1096

Herbert B. Ingram, Jr.:
Direct ..... JA 723
Cross ..... JA 880
Redirect ..... JA 1008
Recross ..... JA 1026

Nicholas J. Grant:
Direct ..... JA 1038
Rebuttal Direct ..... JA 1074
Cross ..... JA 1077
Redirect ..... JA 1090

Volume V

EXHIBITS

PAGE

For Defendant

A ..... E 1
B ..... E 4
D ..... E 4-1
E ..... E 5
F ..... E 9
G ..... E 10
H ..... E 11
I ..... E 12
M ..... E 14
S ..... E 16
V ..... E 16-1

PAGE

Z ..... E 18
AA ..... E 19
AG ..... E 20
AM-1 ..... E 21
AP ..... E 24
AU ..... E 26
[illegible] ..... E 28
BS ..... E 29
BU ..... E 32
BW ..... E 33
BZ ..... E 34
CQ ..... E 34-1
[illegible] ..... E 34-2
CS ..... E 35
CU ..... E [illegible]
CW ..... E 42-1
DH ..... E 42-2
DJ ..... E 42-4
DL ..... E 42-6
DQ ..... E 43
FA ..... E 44
FB ..... E 47
FC ..... E 49
FD ..... E 51
FE ..... E 55

PAGE

FL ..... E 83
FM ..... E 89
FR ..... E 95
GA ..... E 97
GB ..... E 98
GC ..... E 99
GE ..... E 100
IL ..... E 139
IV-1 ..... E 144
IV-2 ..... E 151
IW ..... E 157
IX ..... E 165
KB ..... E 165-1
KC ..... E 167
KN ..... E 167-1
KT ..... E 172

For Plaintiff

1 ..... E 176

Volume VI

2 ..... E 242
3 ..... E 390
4 ..... E 474

Volume VII

	PAGE
5	E 599
6	E 698
7	E 804
8	E 876
10	E 880
11	E 889
12	E 900
14	E 911
15	E 914
16	E 943
21	E 944

Volume VIII

24	E 946
25	E 949
33	E 953
40	E 956
43	E 961
50	E 986
51	E 987
52	E 989
53	E 990
60	E 991
62	E 992
63	E 993

PAGE

64 ..... E 998
65 ..... E 1001
66 ..... E 1002
69 ..... E 1007
70 ..... E 1008
71 ..... E 1009
72 ..... E 1010
73 ..... E 1012
74 ..... E 1023
75 ..... E 1045
88 ..... E 1046
89 ..... E 1047
90 ..... E 1049
91 ..... E 1062
92 ..... E 1063
93 ..... E 1064
94 ..... E 1066
95 ..... E 1068

EXCERPTS FROM

Deposition of Dietrich ..... E 1069
Deposition of Quaas ..... E 1071
Deposition of Broderick ..... E 1096
Deposition of Kapralos ..... E 1114
Deposition of Cook ..... E 1157
Deposition of Yurasko ..... E 1173
Deposition of Patel ..... E 1219

E 599

P.O. Box 1925	P.O. Class INS		PATENT NUMBER 3324515
Assistant examiner Keen	Class 71	Subclass 191	DATE JUN 20 1967
Group No. 113	Filed complete (Date) MAR. 23, 1965	Serial No. 442 727	CLAIMS PRIORITY FOREIGN APPLICATIONS If no claim is made, check here
			Country / Application Date
			Application No. / Patent No.
			Number claims allowed 28 / Print claim(s) 1 / Class 29 / Subclass 196.2

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Title of invention

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

☐ Division of ☐ Continuation of ☐ Substitute for aband. appl. ☐ Continuation-in-part of

APPLICATION		APPLICATION
Serial No.	Filed	Serial No. 543705
Now Patent No.	Granted	Filed 2/14/66

Class No.	Extra claims	Filing fee	Amt.	Transaction	Atty's docket
75	33			108901	METCO 305.4

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CERTIFICATE DEC 5 1967 OF CORRECTION

AUTHORITY TO CHARGE DEPOSIT ACCOUNT FOR [illegible] $

DEPOSIT ACCOUNT NO. 02-[illegible] NO. OF CLAIMS 2

PARTS OF APPLICATION FILED SEPARATELY

[illegible]

[THIS SPACE RESERVED FOR RETENTION LABEL]

[THIS SPACE RESERVED]

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EXAMINED AND PASSED FOR ISSUE

David L. Reck 110 (Division Examiner)

ESTIMATE OF PRINTED PAGES		ISSUE FEE DUE (Class 1)
Drw'g(s)	Spec(s)	
1	11	192

NOTICE OF ALLOWANCE & ISSUE FEE DUE (Div.)

Date mailed JAN 12 1967. [illegible]

E 600

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Hon. Commissioner of Patents
Washington 25, D. C.

ON ALL PAPERS PLEASE
FURNISH OUR FILE NO. [illegible]

Dear Sir:

Re the application of Ferdinand J. [illegible]
Shepard
for PLANT STUNTING MICROTOXICALLY MALEIC [illegible]
REINFORCED POLYMER COMPOSITES
we enclose

(X) Specification Ser. No. [illegible]
(x) Declaration Power of Attorney and Petition Filed [illegible]
(x) 1 Sheet(s) Drawings Group [illegible]
(X) 25 Claim(s) in excess of 20
(x) $[illegible].00 filing fee (covered by enclosed check)
( ) Assignment
( ) $3.00 recording fee (covered by enclosed check)
( ) Priority is hereby claimed on the basis of the following:

Country	Serial No.	Date

Respectfully,

BURGESS, DINKLAGE & SPRUNG

BY [illegible]

E 601

MAIN ROOM MAR 25 1965 U.S. PATENT OFFICE

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

This is a continuation-in-part of copending applications, Serial No. 72,543 filed November 22, 1960; Serial No. 134,544, filed August 16, 1961; Serial No. 237,784 filed October 26, 1962; and Serial No. 343,705, filed February 10, 1964.

This invention relates to the flame spraying of exothermically reacting intermetallic compound forming composites. The invention more particularly relates to the flame spraying of flame spray materials in the form of composites containing two or more components which will exothermically react with each other during the spraying, forming one or more intermetallic compounds, and to a novel group of such composites including powders and wires.

Flame spraying involves the feeding of a heat-fusible material into a heating zone, wherein the same is melted or at least heat-softened, and then propelled from the heating zone in a finely divided form, generally onto a surface to be coated.

The material being sprayed is generally fed into the heating zone in the form of either a powder or a wire (the latter term designating both rods and wires). The spraying is effected in a device known as a heat-fusible material spray gun or a flame spray gun.

In the wire type flame spray gun the rod or wire of the material to be sprayed is fed into the heating zone

formed by a flame of some type, where it is melted or at least heat-softened and atomized, usually by blast gas, and thence propelled in finely divided form onto the surface to be coated. The rod or wire may be a conventionally formed rod or wire of a metal, or may be formed by sintering together finely divided material, or by bonding together finely divided material by means of a plastic binder or other suitable binder which disintegrates in the heat of the heating zone, thereby releasing the material to be sprayed in finely divided form.

For spraying finely divided, i.e., powdered material, a powder type flame spray gun is used in which the powder, usually entrained in a carrier gas, is fed into the heating zone of the gun formed by a flame of some type. The powder is either melted or at least the surface of the grains heat-softened in this zone, and the thus thermally conditioned particles propelled onto a surface to provide a coating. In the powder type spray gun as no "atomizing" energy is required, a separate blast gas is often dispensed with, though the same may be supplied in order to aid in accelerating the particles and propelling them toward the surface to be coated.

The blast gas may be provided for both the wire type and powder type guns to perform the additional function of cooling the workpiece and the coating being formed thereon.

The heat for the heating zone is most commonly

produced from a flame caused by the combustion of a fuel, such as acetylene, propane, natural gas, or the like, using oxygen or air as the oxidizing agent. The heat may, however, also be produced by an electrical arc flame or, in the newer type of guns, by a plasma flame. The plasma flame may in itself constitute part of an electric arc, or, in accordance with a newer development, may be in the form of a "free plasma stream", i.e., a stream of plasma which may be considered independent of the arc as it does not contribute to the electric flow between electrodes.

Heat-fusible material spray guns utilizing electric resistance heating or induction heating as the heat source have also been proposed but have not proven commercially successful except in connection with the spraying of low melting point metals, such as solders, lead and zinc.

Flame spraying in the initial stages of its commercial development was used mostly for the spraying of various metals and was often referred to as metallizing. However, the art of flame spraying extends to the spraying of a much wider group of materials, including higher melting point or refractory metals, ceramics, cermets, and the like, and such materials are of increasing commercial interest.

In the case of spraying heat-fusible materials in the initial form of a rod or wire, the rod or wire is generally of a single composition, i.e., in the form of a specific metal, alloy, ceramic, or the like. While it is true that rods or wires formed from finely divided

material bound together with a binder of plastic or the like, as mentioned above, were known, the binder generally did not take part in the spraying or contribute to the coating, and merely served the purpose of maintaining the rod or wire in shape until fed into the heating zone.

In the case of flame spray powders, while powders formed of several constituents were known, the same were generally in the form of a powder mixture of the individual constituents or, at best, a particle aggregate.

One object of this invention is the spraying of the heat-fusible material in a novel form which allows the obtaining of superior results.

A further object of this invention is a novel group of flame spray materials.

These and still further objects will become apparent from the following description read in conjunction with the drawing in which:

Fig. 1 diagrammatically shows a cross-section of a grain of novel powder in accordance with the invention;

Fig. 2 is a cross-section of a further embodiment of an aggregate grain of novel flame spray powder in accordance with the invention;

Fig. 3 is a diagrammatic cross-section of an embodiment of a novel flame spray wire in accordance with the invention;

Fig. 4 shows a cross-section of a further embodiment of a novel flame spray wire in accordance with the invention; and

Fig. 5 shows a still further embodiment of a novel flame spray wire in accordance with the invention.

In accordance with the invention, the flame spraying is effected with the heat-fusible material in the form of a composite containing at least two components which will exothermically react with each other at the temperatures developed during the spraying, forming an intermetallic compound.

The term "composite" as used herein is intended to designate a structurally integral unit and does not include a mere mixture of components which may be physically separated without any destruction of the structure. Thus, in the case of powder, the term "composite" does not include a simple mixture of individual granules of the separate components, but requires that each of the individual granules contain the separate components which will exothermically react, forming intermetallic compounds. In the case of wire, the individual components must be incorporated in a single wire. In the composite the components must be in intimate contact with each other.

In connection with powders, each grain may consist of an aggregate containing the two components which will exothermically react, forming the intermetallic compound, but preferably the individual grains of the powder are in the form of a clad composite consisting of a nucleus of one of the components and at least one coating layer of the other component. Alternatively, the composite may consist

of separate, concentric coating layers of the two components and a nucleus of still a third material.

In the case of wires, the composites may be in the form of a wire having a coating sheath of one material and a core of the other, alternate coating sheaths of the components and a core of a third material, a wire formed by twising or rolling separate wire strands of the components, a wire consisting of a sheath of one component and a core containing the other component in powder or compacted form, a wire consisting of a sheath of one component and a core containing a compacted powder mixture of this same component material and one or more other components, a wire consisting of a plastic sheath and a core containing a compacted powder mixture of components, etc.

In order for the wires to be satisfactory for spraying, the same must not cavitate at the tip when heated, and should preferably be capable of forming a pointed or slightly tapered tip when being melted and sprayed. Thus, if the wires have an outer layer or sheath of one component and an inner core of another component, the inner core cannot have a lower melting point than the outer sheath, as otherwise the inner core will initially melt, causing cavitation at the tip. For example, if the wire is composed of nickel and aluminum as the exothermically reacting components and is in the form of a core with a coating sheath, the core must be nickel and the coating sheath aluminum,

as otherwise during the spraying the core will initially melt out, causing the cavitation which will interfere with a satisfactory spraying operation. The wire having the melting-point characteristics so as to allow the melting off of the tip without this cavitation, is referred to herein and in the claims as "non-cavitating wire."

As the components any two metallics which may be melted together to form an intermetallic compound in an exothermic reaction may be used. The components should release about 3000 calories per gram atom, and preferably at least 7500 calories per gram atom in the exothermic reaction forming the intermetallic compounds. The term "calories per gram atom" as used herein denotes the number of gram calories which the average atomic weight in grams of the intermetallic compound formed will generate in so being formed. While the components are preferably present in the stoichiometric proportions required for the formation of the intermetallic compound, it is, however, possible to also have an excess of one or the other provided the relative amounts are sufficient to release the quantities of heat indicated above in the formation of the intermetallic compounds.

An extremely large number of metal components are known which can be melted together in an exothermic reaction, forming an intermetallic compound with the generation of heat. Any of these component pairs may be utilized in accordance with the invention, it only being required

that the same be capable of being initially formed into the composite suitable for spraying and that the intermetallic compounds formed therefrom liberate the required amount of heat in the intermetallic compounds-formation and are suitable as components of a sprayed coating. As a general rule, components which will form intermetallic compounds having a higher melting point will liberate sufficient heat to be useful in accordance with the invention. In certain instances, however, components which will form intermetallic compounds which do not have as high a melting point, will also liberate sufficient heat in the exothermic reaction and thus be useful. Preferred components are aluminum with at least one of Co, Cr, Mo, W, Ta, Nb, Ti, or most preferably Ni; or silicon with at least one of Ti, Nb, Cr, W, Co, Mo, Ni or Ta.

While iron itself is not a satisfactory component, the same may be present in addition to another component, which in itself is satisfactory, such as in the form of an alloy therewith. This other component, however, must be present in amount sufficient to form the intermetallic compound with the other component of the composite, with the generation of sufficient heat to aid the spraying operation. Thus, for example, iron which just contains enough alloyed nickel to render the same rust-resistant, does not contain enough nickel for an effective exothermic reaction with aluminum. Generally an alloy of nickel and iron must contain at least about 12% nickel for this purpose.

Fig. 1 shows a composite powder consisting of a nucleus of aluminum and a coating layer of nickel. Fig. 2

shows an aggregate of these components; and Figs. 3, 4, and 5 show various forms of wire containing these components, Fig. 3 showing a wire having an aluminum core with a nickel sheath, Fig. 4 showing a wire made of alternate strands of nickel and aluminum wire, as for example 18 strands of 25 gauge (.019" diameter) nickel wire ~~marked 1~~, and 19 strands of 25 gauge aluminum wire ~~marked 2~~; and Fig. 5 shows a sheath of aluminum filled with granules of nickel and aluminum.

Where one of the component metals is available as a metal hydride, the same may be used in this form rather than as a metal per se. When flame sprayed the hydrogen gas evolved from the hydride produces a reducing atmosphere, which in turn suppresses oxidation of the intermetallic compounds during and immediately after their formation. Thus, for example, in place of titanium, titanium hydride may be used as one of the components.

Also for the purpose of reducing oxidation a metal hydride, such as titanium hydride, may be added in a minor amount to the other components. Thus, for example, 1 - 10% by weight, and preferably 1 - 5% by weight, based on the total of the hydride and other components, may be used.

In addition, the powder granules and the wire may contain other conventional flame spray components, or be sprayed in admixture or in conjunction therewith. Thus, for example, the coated powders may additionally contain other coating layers of other flame spray components or may contain a nucleus of another flame spray material with

alternate coating layers of the components which will exothermically react, forming the intermetallic. In a similar manner, the aggregates or the wires may contain further flame spray components, and in the case of powders, the same may additionally be admixed with any other desired flame spray powder.

The clad powders, in accordance with the invention, may be formed in any known or desired manner, and preferably by the known chemical plating processes, in which coating material is deposited on a seed or nucleus of another material, or in which multiple layers of various materials are built up on the seed material, or in which various materials are co-deposited in a single layer on the seed material.

A mode of forming the clad powders involves the depositing of a metal from a solution by reduction on a seed or nucleus, such as by the hydrogen reduction of ammoniacal solutions of nickel and ammonium sulfate on a seed powder catalyzed by the addition of anthraquinone. It is also possible to form the coating by the use of other known coating processes, such as coating by vapor deposition, by the thermal decomposition of metal carbonyls, by hydrogen reduction of metal halide vapors, by thermal deposition of halides, hydrides, carbonyls, organo metals, or other volatile compounds, or by displacement gas plating and the like.

A preferred and greatly simplified mode of forming the clad powders in accordance with the invention

is the depositing of one component as a coating in the form of a paint on the other component. Thus, one of the components which is to form the coating or cladding, may be dispersed in finely divided form in a binder or lacquer so as, in effect, to form a paint in which this component corresponds to the pigment. The paint is then used to coat core particles of the other component and the binder or lacquer allowed to set or dry. The binder material is preferably a resin which does not depend on solvent evaporation in order to form a dried or set film, and which film will decompose or break down in the heat of the spraying process. The binder, for example, may be a phenolic varnish or any other known or conventional varnish, preferably containing a resin as the varnish solids. The component which is initially mixed with the binder or varnish should preferably be as finely divided as possible, as for example -325 mesh. The other component which constitutes the core should be approximately or only slightly below the particle size ultimately desired for the spray powder. The coating of the core component with the "paint" may be effected in any known or desired manner, and it is simply necessary to mix the two materials together and allow the binder to dry or set, which will result in a fairly free-flowing powder consisting of the core component coated with a cladding of the other component bound in the binder.

The aggregates may be formed by compacting or

briquetting the various components into the individual granules, or into larger aggregates and then breaking these aggregates into the granules.

The wires may be formed in the known conventional manner for forming wires with various components as, for example, by shrinking a sheath on a core, by forming the core with powder, by twisting the component wires, followed by rolling, drawing, swaging, or the like if desired.

In accordance with one mode of manufacture, one of the components may be formed into a tube or sheath and filled with a powder of the other component or a powder comprising a mixture of the two components, or containing additional components. The tube ends are then sealed and the wire reduced to the desired wire diameter by swaging, rolling or drawing. Preferably the powder or powder mixture is first compressed into cylindrical briquettes before being placed in the sheath or core. The sealing of the tube ends after loading with the powder or powder mixture can be effected, for instance, by insertion of a plug, for example of the metal of the sheath, by welding, twisting, crimping, or the like.

Powders in accordance with the invention should have the general over-all shape and size of conventional, flame-spray powders, and thus for example should have a size between -60 mesh and +3 microns and preferably -140 mesh and +10 microns (U.S. Standard screen mesh size). Most preferably the powder should be as uniform as possible in grain size, with the individual grains not varying by more than 250 microns and preferably 75 microns.

Depending on the particular flame spray process and the desired purpose, the composite powders may be sprayed per se or in combination with other different composite powders, or in combination with other conventional flame spray powders or powder components.

While the powders are preferably sprayed, as such, in a powder-type of flame spray gun, it is also possible to combine the same in the form of a wire or rod, using a plastic or similar binder, which decomposes in the heating zone of the gun, or in certain cases the powders may be compacted and/or sintered together in the form of a rod or wire. The wires must have the conventional sizes and accuracy tolerances for flame spray wires, and thus for example may vary in size between 1/4" and 20 gauge, and are preferably of the following sizes: 3/16" ± .0005" - .0025", 1/8" ± .0005" - .0025", 11 gauge ± .0005" - .0025", and 15 gauge +.001", with a smooth, clean finish free from surface marks, blemishes, or defects. The wires are sprayed in the conventional manner, using conventional wire-type flame spray guns.

In combining, in the exothermic reaction, forming the intermetallic compound, the components generate heat in situ in the actual material which is to form at least a part of the coating. This is to be distinguished from flame-spray processes and materials in which heat is generated by a reaction, such as an oxidation reaction, in which a foreign and non-metallic element is introduced and in which undesirable components may be produced. Aside from greatly contributing to the thermal efficiency of the process, the

heat generated in situ in the formation of the intermetallic compound produces novel results, in many instances forming a denser, more adhering coating, having characteristics of at least a partially fused coating. In many instances the coating has self-bonding characteristics, so that special surface preparation, other than a good cleaning, is not required. The spraying in all other respects is effected in the conventional, well-known manner, using conventional flame spray equipment, and the conventional surface preparation may be utilized, if desired. The composites in accordance with the invention may be sprayed in conjunction with, or in addition to, other flame spray materials conventionally used in the art, or may be sprayed in combination or conjunction with the others.

The use of the composites as, for example, the nickel-aluminum composites, will generally improve the bond of the total sprayed material, and thus of the other component or components to the substrate, sometimes making the mixture self-bonding. The particle bond will be improved and the coating will be denser, so that its porosity may be decreased. In general, as little as 10% by weight of the composites in accordance with the invention will be sufficient to substantially improve the bonding characteristics and decrease the porosity of other flame spray materials, such as conventional flame spray metals, alloys or ceramics. There is, of course, no upper limit on the amount, as the composite may be sprayed per se, but generally at least about 20% by weight of the other component is required if

this component is to have a pronounced effect on the characteristics of the coating.

The following examples are given by way of illustration and not limitation:

EXAMPLE 1

(a) An aluminum powder having a particle size between -140 mesh and +325 mesh (U.S. Standard screen size) is coated with nickel in the known manner by the hydrogen reduction of an ammoniacal solution of nickel and ammonium sulphate, using anthraquinone as the coating catalyst. The reduction is effected at a temperature between about 300 and 350° F. in a mechanically agitated autoclave using solutions containing 40-50 grams per liter of nickel and 10-400 grams per liter of $(NH_4)_2SO_4$ and 20-30 grams per liter of NH_3. About .2 gram per liter of anthraquinone is used as the catalyst and the autoclave is pressurized with hydrogen at a pressure of about 300 lbs. p.s.i.g. After the nickel solution is depleted and the aluminum coated with an initial coating of nickel, the solution is discharged from the autoclave and replenished with a fresh solution which need not contain further amounts of the anthraquinone coating catalyst, as the initially formed nickel coating in itself acts as a catalyst. The cycle is continuously repeated until a composite powder

is formed containing about 16 to 13% by weight aluminum and 84 to 82% by weight of nickel, and a size of -100 to +270 mesh.

The powder thus formed is flame-sprayed on a mild steel plate which has been surface-cleaned with emery cloth. The spraying is effected at about 9 inches from the plate, using a powder-type flame-spray gun as described in U.S. Patent 2,961,335, issued November 22, 1960 and sold by Metco Inc. of Westbury, Long Island, under the trade name of "Thermospray" powder gun. The spraying is effected at a rate of 6 to 9 lbs. of powder per hour, using acetylene gas as the fuel at a pressure of 10 p.s.i. and a flow rate of 17 to 25 cu.ft./hr. and oxygen as the oxidizing gas at a pressure of 12 p.s.i. and a flow rate of 29 to 35 cu.ft./hr.

The nickel coating and the aluminum base combine in the heat of the flame with a strong exothermic reaction, forming a mixture of nickel aluminum intermetallic compounds which deposit on the base as a dense, high quality coating which exhibits self-bonding characteristics. A coating layer of .002" - .004" thickness is built up in this manner. The coating may be used as a base material for spraying of further layers of different metals or the like, and

serves as an excellent intermediate bonding layer.

The coating layer may also be built up to a greater thickness as, for example, .010" - .020", for use as an oxygen barrier undercoat, or to even greater thickness as, for example, .020" - .040" or thicker as a wear-resistant - oxidation-resistant surface.

Due to its self-bonding characteristics the sprayed coating will adhere to a base without the conventional surface preparation or roughening, and due to the natural characteristics of a sprayed material, will allow further materials to be sprayed thereon with good bonding. The coating formed from the powder has excellent oxidation-resistant characteristics even at high temperatures and in oxidizing atmospheres, and will for example prevent the oxidation of base materials, such as molybdenum or the like. The sprayed coatings may be used as a lining in metal-melting crucibles or molten metal-handling equipment, and will not be wetted or penetrated by many molten metals, including self-fluxing alloys. Coatings formed of the sprayed material also show good potential as high temperature, wear-resistant coatings.

25

When the example is repeated on a molybdenum rod of 3/16" diameter, with a coating between .010"

± .012" thick, the coated rod may be repeatedly heated to approximately 2000° F. in air, in an electric furnace and cooled to room temperature with no visible oxidation occurring.

Similar results may also be obtained if the composite powder contains 10 ± 45% by weight of aluminum and 55 ± 90% by weight of nickel.

(b) Example 1(a) is repeated, using, however, cobalt in place of the nickel. Comparable results are obtained.

(c) Example 1(a) is repeated, using titanium hydride (TiH_2) powder in place of the aluminum and in an amount of 25 ± 85 weight %, and preferably 60 ± 85 weight % of the total. The coating formed upon spraying is hard and dense, and when sprayed on a smooth, pressed and sintered Al_2O_3 substrate, an excellent bond is formed. The spraying may be effected with an oxygen-hydrogen or oxygen-acetylene flame.

EXAMPLE 2

Example 1 is repeated with the spraying being effected in turn on the following bases and prepared in the following manner:

Low alloy steels and stainless steels, smooth-ground to remove surface contamination; copper and copper base alloys, rough-ground or

light-grit-blasted; aluminum and aluminum base alloys, rough-ground or light-grit-blasted; magnesium, rough-ground or light-grit-blasted; and titanium, rough-ground or light-grit blasted.

In each case when a further material, such as steel, alumina or the like, was sprayed over the coating in the conventional and well known manner, the same was bonded with a tenacious bond, though if this material had been initially sprayed on the surface as prepared in the manner indicated above, a satisfactory bond would not be obtained.

EXAMPLE 3

The nickel-clad powder of Example 1 is mixed with an Al_2O_3 powder having a particle size between 62 microns and 10 microns, in the ratio of about 40% of the nickel-clad powder with 60% by weight of the ceramic. The powder is sprayed, using the gun described in Example 1, on a mild steel plate which has been surface-cleaned by smooth grinding. Spraying is effected at a distance of about 9" from the plate at a rate of about 4 to 8 lbs. of powder per hr., using acetylene at a pressure of 10 lbs. p.s.i. and a flow rate of 17 - 25 cu.ft./hr., and oxygen at a pressure of 12 p.s.i. and a flow rate of 29 - 35 cu.ft./hr.

A self-bonding cermet coating is formed which

showed excellent thermal shock-resistance, hardness, abrasion-resistance, and which strongly inhibited oxidation of the base.

It is possible to vary the percentages of the ceramic in the mixture between 5 and 85% in order to vary the properties of the coating. With an increased amount of the intermetallic compound in the cermet coating formed, the bonding and thermal shock-resistant properties increased, whereas with an increased amount of the ceramic, the hardness and wear-resistant properties of the coating are increased and the thermal conductivity decreased.

EXAMPLE 4

Example 3 is repeated, using the following materials in place of the aluminum oxide:

Zirconia, calcium zirconate, magnesium zirconate, spinel, ceric oxide, hafnium oxide, rare earth oxides, molybdenum disilicide, tungsten silicide, chromium silicide, titanium silicide, tungsten carbide, titanium carbide and chromium carbide.

In each case an excellent coating was formed.

EXAMPLE 5

A nucleus of silicon powder is coated with nickel to form a nickel-clad flame spray powder having a particle size between 100 and 325 mesh

and containing 75 - 85% nickel based on the silicon-nickel total. The composite powder is sprayed with the flame spray gun described in Example 1 on a steel base prepared by lightly grit-blasting, using the spraying conditions as described in Example 1. During the spraying silicon combines with the nickel in an exothermic reaction, greatly enhancing the thermal efficiency of the spraying and producing an excellent coating.

EXAMPLE 6

Titanium is coated with nickel as described in Example 1 to produce a powder having a particle size between 100 and 325 mesh and containing 10 to 50% nickel based on the titanium-nickel total.

The nickel protects the titanium from oxidation during storage and when spraying.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the nickel and titanium combine exothermically in the flame to form a corrosion-resistant coating comprising a nickel-titanium intermetallic compound.

18

EXAMPLE 7

Tellurium powder was coated with copper so as to form a composite having a particle size between 100 and 325 mesh and containing 50 to

80% copper based on the tellurium-copper total.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the copper and tellurium combine to form a new material.

During the spraying heat was evolved upon the combination of the copper and tellurium, increasing the thermal economy of the process.

EXAMPLE 8

The nickel-clad flame spray powder of Example 1 is mixed with about 20% by weight of low pressure polyethylene powder and molded at a temperature of about 212° F. into the form of a rod of 1/8" diameter. The rod is sprayed, using a conventional wire-type flame spray gun sold by Metco Inc. of Westbury, Long Island, as the Metco-type 4-E Gun. The spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu.ft./hr. with oxygen as oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu.ft./hr; with air as a blast gas at a pressure of 40 p.s.i. and a flow rate of 25 cu.ft./min. The end coating produced is similar to the coating produced in Example 1.

EXAMPLE 9

A wire is formed by encasing a core of nickel in a tube of aluminum and drawing to a

size of .125" in diameter plus or minus .002". The wire contains 82 to 84% by weight of nickel based on the aluminum-nickel total.

The wire is sprayed, using a conventional wire type flame spray gun sold by Metco Inc. of Westbury, ~~Long Island~~, as the Metco type 4-E Gun. Spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu.ft./hr. with oxygen as the oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu.ft./hr. Air is used as a blast gas at a pressure of 55 p.s.i. and a flow rate of 30 cu.ft./min. The end coating produced is similar to the coating produced in Example 1.

Similar results are also obtained using 55 - 90% by weight of nickel in the wire.

EXAMPLE 10

A composite wire is formed by winding individual wires of nickel and aluminum to form a stranded wire with a diameter of .125" plus or minus .002". The wire contains 55 to 90% by weight of nickel based on the total Al-Ni. The wire is sprayed in the manner described in Example 9, with identical conditions and coating resulting.

EXAMPLE 11

A silicon powder having a particle size between 140 and 325 mesh is coated with molybdenum in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The molybdenum coating and the silicon base combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

EXAMPLE 12

A molybdenum powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light

grit-blasting. The spraying is effected at a point five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, ~~Long Island, New York~~, under the trade name of Type 2MB Plasma Flame Gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using a mixture of argon and hydrogen gas as the plasma gas, with argon at a pressure of 100 p.s.i. and a flow rate of 115 cu.ft./hr., and hydrogen at 50 p.s.i. and a flow rate of 25 cu.ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu.ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57-62 volts.

The molybdenum base and silicon coating combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

EXAMPLE 13

A silicon powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner, and a composite powder is formed containing about 48 to 85% chromium

and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The chromium coating and the silicon base combine in the heat of the flame, forming a chromium-silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

57

EXAMPLE 14

A chromium powder having a particle size between 140 and 325 mesh is coated with silicon in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type 2MB Plasma Flame

gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu.ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu.ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57-62 volts.

The chromium base and silicon coating combine in the heat of the flame, forming a chromium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

EXAMPLE 19

A zirconium powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner and a composite powder is formed containing about 45% zirconium and 60% chromium by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material in the manner described in Example 1.

The chromium coating and the zirconium base combine in the heat of the flame, forming a chromium zirconium intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures.

EXAMPLE 16

A titanium powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 65% titanium and 35 to 65% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, ~~Long Island~~, New York, under the trade name of Type 2MB Plasma Flame Gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu.ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu.ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of

400-500 amperes at 57-62 volts.

The titanium base and silicon coating combine exothermically in the heat of the flame, forming a titanium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

EXAMPLE 17

A dysprosium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 60 to 75% dysprosium and 25 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The aluminum coating and the dysprosium base combine in the heat of the flame with a strong exothermic action, forming a dysprosium aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

EXAMPLE 18

A lanthanum powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 70 to 75% lanthanum and 25 to 30% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the lanthanum base combine exothermically in the heat of the flame with a strong exothermic action, forming a lanthanum aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

EXAMPLE 19

A chromium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed consisting of 60 to 62% chromium and 38 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the chromium coat combine in the heat of the flame with a str... exothermic action, forming a chromium aluminu... intermetallic compound which deposits on the work as a dense, high quality coating of very high melting point and excellent oxidation-r...

EXAMPLE 20

Example 19 is repeated except that the com... posite powder is formed with an aluminum core and chromium coating. Identical results are obtained.

EXAMPLE 21

The nickel-clad aluminum composite prepared in Example 1 is mixed with cobalt bonded tungsten carbide particle powder having a particle size range of -140 mesh +10 microns, and preferably -140 +325 mesh in proportions of:

a) 80 weight percent tungsten carbide to 20 weight percent of the composite.

b) 20 weight percent of the carbide to 80 weight percent of the composite, and

c) preferably 50 weight percent each of the tungsten carbide and composite.

The powder mixtures are each flame-sprayed on a mild steel plate which has been surface-cleaned by grinding or very light sand-blast cleaning. The spraying is effected at about 8 - 9 inches from the plate, using a powder-...

flame-spray gun as described in U.S. Patent 2,961,335 issued November 22, 19[illegible], and [illegible] Metco Inc. of Westbury, Long Island, New York, under the trade name of "Thermo-Spray" flame gun. The spraying is effected at a rate of 6 to 10 lbs. per hour using acetylene gas as the fuel at a pressure of 12 p.s.i. and a flow rate of 20 to 30 cu.ft./hr. and oxygen as the oxidizing gas at a pressure of 14 p.s.i. and a flow rate of 30 to 40 cu.ft./hr.

The nickel-aluminum composite powder in the mixture reacts exothermically in the flame to provide the self-bonding properties of the mixture and, being fully molten on its contact with the substrate, becomes the matrix which bonds the tungsten carbide particles together in the coating.

Used as sprayed, or finished by [illegible] grinding procedure, the resultant coating is a highly wear-resistant coating material, applicable to virtually any backing material subject to the limitations of the commercially used self-fluxing alloy matrix materials which must be fused at approximately 1[illegible] F.

Example 22

Example 21 is repeated except that in place of the grade of tungsten carbide

carbide grains with lower cobalt content and sharp, angular shape are used.

The powder was sprayed in the manner described in Example 21. The sharp, angular edges of the initial tungsten carbide particles were retained in the coating.

The deposited coating may be suitably finished by grinding for use as a wear-resistant coating or used as deposited where the coated article is to be used as a hone or lap, the sharp edges of the carbide inclusions constituting the abrading or cutting edges.

EXAMPLE 23

Example 22 is repeated except that in place of the tungsten carbide grains described, cobalt-bonded tungsten carbide particles of sharp, angular shape were used which were first coated with nickel in the manner described in Example 1, so as to produce nickel-clad particles having a size between 100 and 325 mesh and containing from 20 - 50% nickel based on the tungsten carbide-nickel total.

EXAMPLE 24

The nickel-clad aluminum composite described in Example 1 is mixed with a columbium (niobium) powder of size between -120 mesh and

+10 microns and preferably -140 +325 mesh in the proportions of 60 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and when properly finished, by grinding or other means, is a highly wear-resistant, hard coating.

EXAMPLE 25

The nickel-clad aluminum composite described in Example 1 is mixed with a molybdenum powder of a size between -120 mesh and +10 microns and preferably -140 +325 mesh in the proportions of 65 weight percent molybdenum to 35 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and when properly finished, by grinding or other means, presents a highly wear-resistant, hard surface.

EXAMPLE 26

Example 21 is repeated except in place of the tungsten carbide, other carbides such as titanium carbide, tantalum carbide, columbium

carbide, chromium carbide and mixtures of the various carbides are used.

EXAMPLE 27

The nickel-clad aluminide core composite from Example 21 is mixed with aluminum powder in the mesh size range -100 +325 mesh, and preferably in the -170 +325 mesh size range in the proportions of 80 weight percent nickel aluminum composite to 20 weight percent aluminum.

The mixture was sprayed in the manner described in Example 21. The coating as deposited consists of an intimate mixture of the flame-reacted nickel aluminide and aluminum securely bonded to the base and particle to particle within the coating.

Upon heat-treating in the temperature range 1250° F. to 1500° F. in reducing atmosphere, eg. hydrogen for instance, the nickel aluminide and aluminum combine to form a dense, homogeneous coating fused to the base material which can be used for "cathodic" protection of iron and steel subject to water and salt-water corrosion.

EXAMPLE 28

The nickel-clad aluminum composite powder of Example 21 is mixed with Monel powder of a size between -100 mesh and +10 microns, and preferably between -140 and +325 mesh in the propor-

5b

35 weight percent composite to 65 weight percent Monel.

The powder mixture was sprayed in the manner described in Example 21. The resultant coating has self-bonding to a wide variety of substrate materials and the inclusion of the nickel-aluminum composite, the components of which combine exothermically in the flame to provide the self-bonding ability of the mixture, contributes to increased particle to particle bonding within the coating and decrease the permeability of the coating.

EXAMPLE 29

Example 28 is repeated except that nickel and stainless steel powders are substituted for Monel.

EXAMPLE 30

Example 28 is repeated except that chromium is substituted for the Monel.

The resultant coating when properly finished by grinding or other means, shows high resistance to abrasion, wear, and galling by other metals and is an excellent bearing surface.

EXAMPLE 31

Finely divided aluminum powder (-325 mesh) was blended with a phenolic varnish having approximately

50% solid contents so as to form a mixture having the consistency of a heavy syrup and containing 60% by weight of the metallic aluminum.

100 grams of this varnish aluminum powder mixture was added to 240 grams of nickel powder having a size between -200 and +325 mesh, and the two were thoroughly mixed, with the mixing continued until the varnish dried, leaving a fairly free-flowing powder in which all of the nickel core particles were clad with a dry film, which consisted of aluminum particles bonded to each other and to the core material by the phenolic binder. The powder is then warmed to 250° F. to insure complete drying. There were some minor agglomerates which were screened out and hammer-milled to reduce the same to a -100 mesh powder. The end powder consisted of approximately 15 weight % aluminum and 85 weight % nickel due to the loss of some aluminum during the milling. The powder is sprayed in the manner described in Example 1 producing a similar coating having, however, more than twice the tensile strength of the coating produced in Example 1.

EXAMPLE 32

(a) A mixture of 6 weight % aluminum and 94 weight % nickel powder are thoroughly blended and pressed together in the form of cylindrical briquettes which are loaded into an aluminum tube

of .375" outside diameter, after which the tube ends are welded closed. The 3/8" diameter [illegible] stock is then swaged to 1/4" diameter, then to a 3/16" diameter and then to a 1/8" finished wire diameter. The wire is then annealed and coiled. The wire is then sprayed, using the conventional wire type flame spray gun sold by Metco Inc. as the Metco Type 4-E Gun. Spraying is effected, using acetylene at a pressure of about 15 lbs. p.s.i. and a flow rate of 37 cu.ft./hr. and oxygen as the oxidizing gas at a pressure of 30 lbs. p.s.i. and flow rate of 75 cu.ft./hr. Air is used as the blast gas at a pressure of 35 lbs. p.s.i. and flow rate of 30 cu.ft./min. The wire is sprayed at a rate of 5 ft. per minute. The spray material is deposited on a surface of ground and machine-finished, cold rolled steel with a tensile bond strength of 3820 lbs. p.s.i. The sprayed coating is hard and dense; it is wear- and oxidation-resistant and it also could serve as a base for further spraying.

(b) Example 32(a) is repeated except that chromium is used in place of the nickel [illegible] in amounts of from 24 - 95 weight %, based on the total of the aluminum and chromium. Spraying results in a high quality coating which has good bonding properties and is resistant to oxidation at high temperatures.

(c) Example 32(a) is repeated, using columbium powder in place of the nickel powder in amounts of from 40 - 90 and preferably 50 - 55 weight %, based on the total of the columbium and aluminum. The sprayed coating formed is a high quality coating which is resistant to oxidation at high temperatures and may be used to protect tantalum and molybdenum bases from oxidation.

(d) Example 32(a) is repeated, using tantalum powder in place of the nickel powder in amounts of 40 - 90 weight % and preferably 65 - 75 weight % of tantalum, based on the total of tantalum and aluminum. The sprayed coating is a dense, high quality coating which is self-bonding and is resistant to oxidation at high temperatures.

(e) Example 32(a) is repeated, using boron powder in place of the nickel powder in amounts of 40 - 90 weight %, based on the total of boron and aluminum. The resulting sprayed coating is self-bonding and is resistant to oxidation at high temperatures.

(f) Example 32(c) is repeated except that the powder additionally contains 0.5 to 5 weight % of boron, and/or 0.5 to 5 weight % of silicon, based on the total of the components. The coating formed is similar to that obtained in Example 32(c) except that on heating to high temperatures,

a very thin, dense, adherent, protective oxide film forms on the surface of the intermetallic compound formed, which is resistant to spalling due to thermal shock, and which is believed self-healing.

(g) Example 32(a) is repeated except that tungsten carbide containing 12% binder and having a particle size below -140 mesh is added in amounts of 5 - 70 weight %, based on the total of the components. The resulting coating is a dense, extremely wear-resistant coating, which has self-healing properties. This example may be further repeated, using in place of the tungsten carbide specified, crystalline tungsten carbide, aluminum oxide, diamonds or any other abrasive material.

(h) Example 32(a) is repeated. However, 1 - 10% by weight and preferably 1 - 5% by weight of titanium hydride of a size below -100 mesh and preferably below -325 mesh, based on the total of the components, is added to the core material. The results are the same as indicated in Example 32(a) except that the coating formed is of improved bonding strength, containing considerably less oxide inclusions. In place of the titanium hydride other metal hydrides may be used.

(i) Example 32(a) is repeated except that the nickel powder is replaced with a nichrome powder consisting of a chromium alloy containing 80% nickel and 20% chromium. When sprayed the wire gives a

dense, self-bonding coating which is extremely oxidation-resistant.

(j) Example 32(a) is repeated except that the nickel powder is replaced with a powder mixture consisting of 80% by weight nickel and 20% by weight chrome. When sprayed the wire gives a dense, self-bonding coating which is highly oxidation-resistant.

EXAMPLE 33

Table I below gives examples of further component pairs which may be used to form the powders and/or wires in accordance with the invention.

Each of the component pairs as listed in Table I below may be formed into a composite powder or wire as described above, and when flame-sprayed will exothermically react, forming an intermetallic compound and high grade coating. Thus, the component pairs may be formed into clad powders as described in Example 31 and sprayed as described therein, or formed into a composite wire as described in Example 32 and sprayed as described therein.

E 642

Table I

Al Ce	As In	Bi Mg	In Te	Pb Ru
Al As	As Mg	Bi Na	In Ru	Pb Se
Al Au	As Zn	Bi Se	K Sb	Pb Tl
Al B	B Y	Bi Te	K Se	Pd U
Al Ba	B Ca	Bi Th	K Sn	Pr Sn
Al Ca	B Cr	Cd Pb	K Tl	Pr Tl
Al Ce	B Hf	Ca Sn	La Pb	Sb Zr
Al Co	B Nb	Ca Tl	La Sb	Se Sn
Al Cr		Ca Y	La Sn	Se Te
Al La			La Tl	Se Tl
Al Li	B Pt	Ce In	La Zn	Cu Te
Al Mo	B V	Ce Mg	Li Pb	Si Tl
Al Nb	B W	Ce Pb	Li Sb	Si U
Al Ni	B Zr	Ce Si	Li Sn	Si V
Al Pr	Ba Bi	Ce Sn	Li Tl	Si Zr
Al Ti	Ba Pb	Ce Tl	Li Zn	Sn Te
Al Zr	La Sb	Ce Zn	Mg Si	Sn U
Al Sb	Be Co	Cs Na	Mg Sn	Sr Tl
Al Se	Be Cr	Cs Pr	Na Pb	Te Tl
Al Ta	Be Ni	Cs Sb	Na Sb	Tl Y
Al Te	Be Np	Cs Te	Na Se	Mo Re
Al U	Be Pu	Cs U	Na Sn	Ta Th
Al V	Be U	Cs Mg	Na Te	V Zr
Al W	Be Zr	Cs Nb	Na Tl	Tl Y
As Cd	Bi Ca	Cs Zr	Nb Si	Cr Ir
As Ga	Bi Cr	Ir Th	Ni Th	Cr Pt
	Bi K	Ir In	Pb Pr	Cr Zr

2133

Table I (continued)

Mg Te

Ni Te

Si Th

Si W

Co Si

Mo Si

Ni Si

Si Ti

While the invention has been described in detail with reference to certain specific embodiments, various changes and modifications which fall within the spirit of the invention and scope of the appended claims will become apparent to the skilled artisan. The invention therefore is only intended to be limited by the appended claims or their equivalents, wherein we have endeavored to claim all inherent novelty.

We claim:

1. In the flame spray process in which a heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in such condition out of said zone in finely divided form, the improvement which comprises passing the heat-fusible material into said zone in the form of a composite comprising at least two components which exothermically react with each other at the temperature developed in the heating zone, forming an intermetallic compound.

2. Improvement according to claim 1 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.

3. Improvement according to claim 1 in which said components are components which exothermically react with each other, with the release of at least 7,300 gram calories per gram atom.

4. Improvement according to claim 1 in which one of said components is aluminum and the other is nickel.

5. Improvement according to claim 4, in which said aluminum is present in amount of about 10 to 45% by weight, based on the total of nickel and aluminum.

6. Improvement according to claim 1 in which said components are component pairs selected from the group listed in Table I above.

7. Improvement according to claim 1 in which said composite contains at least one additional flame spray material.

8. Improvement according to claim 1 in which said composite is sprayed in conjunction with at least one further flame spray material.

9. In the flame spray process in which heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form, the improvement which comprises passing the heat-fusible material into said zone in the form of individual clad powder particles comprising a nucleus and a coating layer which will exothermically react with the nucleus at the temperature developed in the heating zone, forming an intermetallic compound.

10. Improvement according to claim 9 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.

11. Improvement according to claim 9 in which said components are components which exothermically react with each other, with the release of at least 7,500 gram calories per gram atom.

12. Improvement according to claim 9 in which said nucleus is aluminum and said coating layer is nickel.

13. Improvement according to claim 12 in which said aluminum is present in amount of about 10 - 40%, based on the total of nickel and aluminum.

14. Improvement according to claim 9 in which said nucleus and coating layers are selected from the group consisting of the pairs listed in Table I.

15. Improvement according to claim 9 in which said coating layer consists of fine particles bound to said nucleus by a binder.

16. Improvement according to claim 9 in which said clad powder particles are in admixture with another flame spray powder.

17. In the flame spray process in which heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form, the improvement which comprises passing the heat-fusible material into said zone in the form of a composite, non-cavitating wire or ribbon of at least two components which exothermically react with each other at the temperatures developed in the heating zone forming an intermetallic compound.

18. Improvement according to claim 17 in which said components are components which exothermically react with each other, with the release of at least 3,000 calories per gram atom.

19. Improvement according to claim 17 in which said components are components which exothermically react with each other, with the release of at least 7,500 calories per gram atom.

20. Improvement according to claim 17 in which one of said components is aluminum and the other nickel.

21. Improvement according to claim 20 in which the aluminum is present in amount of about 10 - 45% by weight, based on the total of nickel and aluminum.

22. Improvement according to claim 17 in which said components are component pairs selected from the group listed in Table I above.

23. Improvement according to claim 17 in which said wire is in the form of a sheath of one component containing a powder of the other component, said sheath being of a component having a lower melting point than the other component.

24. Improvement according to claim 23 in which said sheath is an aluminum sheath and in which said core is a compacted mixture of aluminum and nickel powder.

25. Improvement according to claim 17 in which said wire is a multi-strand wire with individual strands of said components.

1
~~24.~~ A flame spray material ~~suitable for use in the process of claim~~ in a form suitable for flame spraying, formed comprising a composite of at least two metal components which exothermically react with each other when melted, forming an intermetallic compound.

2
~~25.~~ A flame spray material ~~suitable for use in the process of claim~~ in a form suitable for flame spraying, formed comprising a composite of at least two metal components which exothermically react with each other when melted, forming an intermetallic compound with the release of at least 3,000 gram calories per gram atom.

3
~~26.~~ A flame spray material ~~suitable for use in the process of claim~~ in a form suitable for flame spraying, formed comprising a composite of at least two metal components which exothermically react with each other when melted, forming an intermetallic compound with the release of at least 7,500 gram calories per gram atom.

4
~~27.~~ A flame spray material ~~suitable for use in the process of claim~~ in a form suitable for flame spraying, formed comprising a composite of aluminum and nickel.

5 4
~~28.~~ Composite according to claim ~~27~~ in which said aluminum is present in amount of about 10 - 45%, based on the total of nickel and aluminum.

6. ~~31.~~ Composite according to claim ~~26~~ 1 in which said components are component pairs selected from the group listed in Table I above.

7 ~~32.~~ A flame spray powder in the form of individual clad particles comprising a metal nucleus and at least one coating layer of a metal differing from said nucleus and exothermically reactive therewith when melted together, forming an intermetallic compound.

8 ~~33.~~ A flame spray powder in the form of individual clad particles comprising a metal nucleus and at least one coating layer of a metal differing from said nucleus and exothermically reactive therewith when melted together, forming an intermetallic compound, with the release of at least 3,000 gram calories per gram atom.

9 ~~34.~~ A flame spray powder in the form of individual clad particles comprising a metal nucleus and at least one coating layer of a metal differing from said nucleus and exothermically reactive therewith when melted together, forming an intermetallic compound, with the release of at least 7,500 gram calories per gram atom.

10 ~~35.~~ A flame spray powder according to claim 7 in which said metal nucleus and metal differing from said nucleus are component pairs selected from the group listed in Table I above.

11 ~~28.~~ A flame spray powder according to claim ~~27~~ 7 in which said coating layer is in the form of a finely divided powder bound to the nucleus by a binder.

12 ~~37.~~ A flame spray powder in the form of individual clad particles comprising a nucleus of aluminum and a coating layer of nickel.

13 ~~38.~~ Powder according to claim ~~37~~ 12 in which said aluminum is present in amounts of about 10 - 45%, based on the total of nickel and aluminum.

14 ~~39.~~ A flame spray powder in the form of individual clad particles comprising a nucleus of nickel and a coating layer of finely divided aluminum particles bound to the nucleus with a binder.

15 ~~40.~~ A non-cavitating flame spray wire ~~suitable for use in the process of claim 1~~, comprising two separate ~~reactive~~ components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound.

16 ~~41.~~ A non-cavitating flame spray wire ~~suitable for use in the process of claim 1~~, comprising two separate ~~reactive~~ components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound, with the release of at least 7,500 gram calories per gram atom.

17. A non-cavitating flame spray wire ~~suitable for use in the process of claim~~, comprising two separate components differing from each other and capable of exothermically reacting with each other when melted together, one of said components being aluminum and the other nickel.

18. A flame spray wire ~~suitable for use in the process of claim~~, comprising two separate components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound, with the release of 7,500 gram calories per gram atom, said components being component pairs selected from the group listed in Table above.

19. A flame spray wire ~~suitable for use in the process of claim~~, comprising a sheath of a first component and a powder core of at least one second component, said first and second components being capable of exothermically reacting with each other when melted together, with the release of at least 7,500 gram calories per gram atom.

20. A flame spray wire according to claim 19 in which said sheath is aluminum and said core a mixture of aluminum and nickel powder.

21. A flame spray wire [illegible] process of claim 1, comprising individual [illegible] separate metal components differing from each other [illegible] of exothermically reacting with each other when melted together, forming an intermetallic compound, with the release of at least 7,500 gram calories per [illegible]

47. Improvement according to claim [illegible] heat-fusible material additionally [illegible]

43. Process according to claim [illegible] said components is at least partially [illegible] hydride.

22 48. Flame spray material according to claim [illegible] additionally containing a metal hydride.

23 51. Flame spray material according to claim 1 in which one of the said components is at least partially in the form of a hydride.

24 51. Flame spray material according to claim 1 additionally containing a member selected from the group consisting of boron, silicon and mixtures thereof.

25 52. A flame spray material [illegible] the process of claim 1, comprising a composite in a form suitable for flame spraying at least two metal components which exothermically react with each other when melted, said components being [illegible] pairs selected from the group consisting of Al Cr, Al Co, Al Mo, Al W, Al Ta, Al Nb, Al Ti, Al Ni, Si Mg, Si Cr, Si W, Si Co, Si Mo, Si Ni, and Si Ti.

26 ~~53.~~ A flame spray material according to claim 25 in the form of a powder.

27 ~~54.~~ A flame spray material according to claim 25 in which one of the components is in the form of a coating on the other component.

28 ~~55.~~ A flame spray material according to claim 25 in the form of a wire.

E 654

DECLARATION, POWER OF [illegible]

We, FERDINAND J. DITTRICH and ARTHUR P. SHEPARD, declare that we are respectively citizens of United States, residing respectively at 2457 New Place, Bellmore, Long Island, New York, and 29-01 - 159th Street, Flushing, Long Island, New York; that we have read the foregoing specification and claims and verily believe that we are the original, first and joint inventors of the improvement in FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES described and claimed therein; that the present application in part discloses and claims subject matter disclosed in our earlier filed pending applications, Serial No. 72,543 filed November 22, 1960; Serial No. 134,564 filed August 16, 1961; Serial No. 237,786 filed October 31, 1962; and Serial No. 343,705 filed February 10, 1964; that as to the subject matter of this application which is not in said earlier applications we do not know and do not believe that the same was ever known or used before our invention thereof or patented or described in any printed publication in any country before our invention thereof or more than one year prior to said earlier applications, or in public use or on sale in the United States for more than one year prior to said earlier applications; that said common subject matter has not been patented before the dates of said earlier applications in any country foreign to the United States on application filed by us or our legal representatives or assigns more than twelve months prior to said applications; that as to the subject matter of this application which is not common to said earlier applications, we do not know and do not

5H

believe that the same was ever known or used before our invention thereof or patented or described in any printed publication in any country before our invention thereof or more than one year prior to this application, or in public use or on sale in the United States for more than one year prior to this application, and that said subject matter has not been patented in any country foreign to the United States on an application filed by us or our legal representatives or assigns more than twelve months prior to this application; and that no application for patent on said invention has been filed by us or our representatives or assigns in any country foreign to the United States, except as follows: Argentina, filed September 14, 1961; Belgium, filed November 21, 1961; France, filed November 17, 1961; Spain, filed September 29, 1961; Australia, filed September 19, 1961; Canada, filed November 8, 1961; Germany, filed October 24, 1961; Great Britain, filed September 14, 1961; Holland, filed October 13, 1961; India, filed August 22, 1961; Italy, filed September 27, 1961; Japan, filed November 22, 1961; Mexico, filed October 20, 1961; Sweden, filed October 27, 1961; Switzerland, filed October 31, 1961; India filed May 21, 1963.

And we hereby appoint BURGESS, DINKLAGE & SPRUNG, Registration No. 15,379, a firm composed of Robert D. Dinklage and Arnold Sprung, of 605 Third Avenue, New York, New York 10016, our attorneys with full power of substitution and revocation to prosecute this application and to transact all business in the Patent Office connected therewith.

55

WHEREFORE we pray that Letters Patent be granted to us for the invention or discovery described and claimed in the foregoing specification and claims, and we hereby subscribe our names to the foregoing specification and claims, declaration, power of attorney, and this petition.

The undersigned petitioners declare further that all statements made herein of their knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Inventor's full name FERDINAND J. [illegible]

Date 22 March 1965 (Signature)

Post Office Address: 2457 New [illegible]
New York.

Inventor's full name ARTHUR P. [illegible]

Date 22 Mar '65 (Signature)

Post Office Address: 29-01 - 150th [illegible]
Island, New York.

2.9/191.2

E 657

PRINT OF DRAWING AS ORIGINALLY FILED

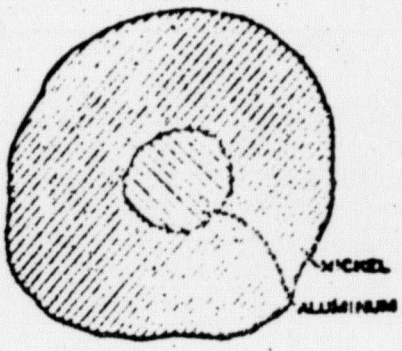

Fig. 1

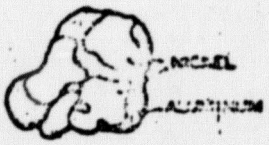

Fig. 2

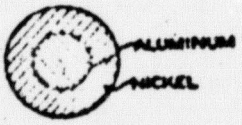

Fig. 3

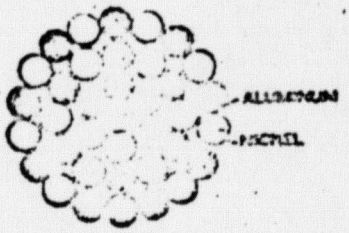

Fig. 4

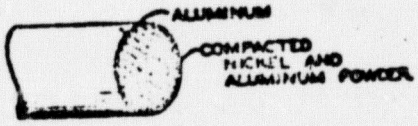

Fig. 5

INVENTORS
FERDINAND J. DITTRICH
ARTHUR R. SHERWOOD

BY Burgess, Dinklage & Sprung

ATTORNEYS

APR 9 1965 U.S. PATENT OFFICE

E 658

60-18

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A3/1p.

IN THE UNITED STATES PATENT OFFICE

Applicant(s) : Ferdinand J. Dittrich, et al.

Serial No. : 442,727

Filed : March 25, 1965

Group 160

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES.

April 8, 1965

Hon. Commissioner of Patents
Washington, D.C. 20231

Sir:

Account No. 02-4740

You are hereby authorized to furnish us with the following references cited in future Office Actions in the above application. Charge the cost thereof to the above account.

XXXXXXXX) U. S. patents
2 copies)

XXXXXXXXX) Foreign patents
2 copies)

XXXXXXXX) Literature references
2 copies)

Respectfully,

BURGESS, DINKLAGE & SPRUNG

BY _____
Attorneys for Applicant(s)

E 659

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al

Serial No. : 442 727 Group 160

Filed : March 25, 1965

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

May 12, 1965

Hon. Commissioner of Patents
Washington, D. C.

Sir:

The following is an amendment before the first Office Action.

In the Table on page 42, cancel "H V" in column 3, next to the last line.

REMARKS

The above corrects an obvious error. Hydrogen, of course, is not a metal.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By: _____
Attorneys for Applicants

E 660

Applicants : Ferdinand J. [illegible]

Serial No. : 442,727

Filed : March 23, 1942

For : [illegible]

Hon. Commissioner of Patents

Washington, D. C.

Sir:

Supplementing the [illegible]

above-entitled application, [illegible]

follows:

Page 42, Table I, colu[illegible]

[illegible]

[illegible]

E 661 Paper No. 5

ADDRESS ONLY THE COMMISSIONER OF PATENTS WASHINGTON, D.C. 20231

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

In Reply Please Refer To Group 150

Burgess, Dinklage and Sprung
605 Third Avenue
New York, N. Y. 10016

Applicant: Ferdinand J. Zletrich et al.
Ser. No. 442,727
Filed Mar. 25, 1965
FLAME SPRAYING EXOTHERMICALLY REACTING [illegible] METALLIC COMPOUND FORMING COMPOSITES

MAILED
OCT 22 1965
U.S. PATENT OFFICE

Cited References Charge Date (if applicable)	
Deposit Account No. 02-4740	No. of Copies 2

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

This application has been examined.

Patents cited toshow classification:

I.	3,121,643	2/1964	Eisenberg	117-105.2
	3,135,626	6/1964	Moen et al.	117-105.2
II.	1,379,063	5/1921	Van Allen	29-191
(5)	2,933,415	4/1961	Homer	29-191

Restriction to one of the following inventions is required:

I. Claims 1 to 25, 47 and 48 drawn to a process of flame spraying, classfied with the Eisenberg and Moen et al. patents.

II. Claims 26 to 46 and 49 to 55 drawn to a metal stock material, classified with the Van Allen and Homer patents.

The inventions as grouped above are distinct each from the other, because the metal material of Group II has different utility than that specifically claimed in the flame spraying of Group I. For example a powder could be used in the fabrication of metal parts from

the compressed compacted powder, in a sintering process or as were in anchoring, sealing or as an electrical conductor.

Restriction for examination purposes as indicated is proper since the inventions as claimed are distinct and have both separate status in the art and divergent fields of search.

Applicants are advised that their response to be complete must indicate a provisional election of one of the above inventions identified as I and II. (See Rule 143.)

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS ACTION IS SET TO EXPIRE TWO MONTHS FROM THE DATE HEREOF.

Richard Plume
Examiner

Ag.
A.Golian/meb
WO 7-2867

E 663 Metc . 5.4

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al

Serial No. : 442 727 Group 160

Filed : March 25, 1965

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUNDS FORMING COMPOSITES

November 12, 1965

Hon. Commissioner of Patents
Washington, D. C.

Sir:

The following is in response to the Office Action dated October 22, 1965.

REMARKS

The Examiner's requirement for restriction is hereby traversed and it is respectfully requested that the same be reconsidered and withdrawn on the ground that claims 26 to 46 and 49 to 55 are limited to a flame spray material such as wire or powder, which is only intended for use in the process of flame spraying as set forth in the claims of Group I.

While the Examiner in his Action indicates other uses for the material outside of the flame spray field, it should be noted that the claims are limited to a flame spray material and to the applicants' best knowledge the material claimed in the claims of Group II only has real suitability as a flame spray material, the reactivity of the components being specific and tailored for this p[illegible],

In accordance with Rule 143, Invention II is provisionally elected for further prosecution. Claims 26 t[illegible] 46 and 49 to 55 fall under this provisional election.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By: [illegible]

E 665

Paper No. 9

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

Burgess, Dinklage and Sprung
605 Third Avenue
New York, New York 10016

In Reply Please Refer to the Following	110
Applicant: Ferdinand J. Dittrich et al.	
Ser. No. 442,727	MAILED MAR 10 1966
Filed: March 25, 1965	
For: FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES	
SHORTENED TIME FOR REPLY	

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

Responsive to the Letter filed November 16, 1965.

Additional references made of record:

2,853,403	9/58	Mackiw et al.	117-100
2,884,688	5/59	Herz	75-170
2,910,356	10/59	Grala et al.	75-170
3,025,182	3/62	Schrewelius	117-105
3,050,409	8/62	Bayer	117-2

Reconsideration of the restriction requirement has been made, but the restriction requirement is deemed sound, is affirmed and is made final. No reason is seen why the product claims could not be used in the way suggested by the Examiner.

The drawing is objected to by the Draftsman as informal because one inch border line is required. It is admitted for examination purposes only. Correction is required but may be deferred until a claim is found allowable. The order for correction should be made in a separate letter to the Draftsman.

Claims 26-46 and 49-55 are rejected for failing to particularly point out and distinctly claim the invention as required in 35 U.S.C. 112. The phrase "for use in the process of claim 1" should be cancelled. The words "nucleus"

"components", etc., are too broad because they cover materials not contemplated by the specification. The phrases "a material differing from said nucleus" and "exothermically react with each other" are functional because they define the material in terms of the result desired, not what produces the desired result. The term "containing" leaves the claim open for the inclusion of unspecified elements in major amounts. Furthermore, the ranges of elements are unknown in the claims, thus the claims are indefinite. The phrase "listed in Table I above" is indefinite. The above are only exemplary of the present condition of the claims.

Claims 26-46 and 49-55 are rejected under 35 U.S.C. 103 as unpatentable over Bayer in view of Schrewelius, Herz, Grala et al, and Mackiw et al. The basic reference discloses exothermically reacting metal powders. Grala et al teaches that nickel and aluminum are exothermically reacting elements. Schrewelius teaches that it is old to add boron to flame-spray powders. Herz teaches that it is old and well known to have powder metals for flame spraying in hydride form. Mackiw et al shows that it is old to form composites of metal powders by having a metal coating covering a metal nucleus. No invention is seen in substituting nickel and aluminum or other elements known to be exothermically reactive in the composition of the basic reference. Or in adding boron a well known fluxing element or in having

the metals in the form of hydrides or in employing the coated composite because all these are taught by the secondary references to be old and well known in the art and the applicants have produced no new and unobvious results.

No claim is allowed.

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS ACTION IS SET TO EXPIRE THREE MONTHS FROM THE DATE OF THIS LETTER.

David L. Rack

DAVID L. RACK

EXAMINER

ROD

RODean:mb

WO7-3621

E 668

IN THE UNITED STATES PATENT OFFICE

Applicant : Ferdinand J. Dittrich et al

Serial No. : 442 727 RECEIVED Group 11[illegible]

Filed : March 25, 1965 JUN - 1 1966

For : FLAME SPRAYING [illegible] MATERIAL [illegible] METALLIC [illegible]

May 24, 1966

Hon. Commissioner of Patents
Washington, D. C.

Sir:

The following is in response to the Office Action [illegible] April 15, 1966. Kindly enter the following amendment:

Claim 26, lines 1 and 2, cancel "suitable for use in the process of claim 1", line 2, cancel "containing" and substitute -- in a form suitable for flame spraying, formed of --

line 3, after "two" insert --metal --.

Claim 27, lines 1 and 2, cancel "suitable for use in the process of claim 1", line 2, cancel "containing" and substitute -- in a form suitable for flame spraying formed of --

line 3, after "two" insert -- metal --.

Claim 28, lines 1 and 2, cancel "suitable for use in the process of claim 1", line 2, cancel "containing" and substitute -- in a form suitable for flame spraying formed of --

Line 3, after "two" insert -- metal --.

Claim 29, lines 1 and 2, cancel "suitable for use in the process of claim 1", line 2, cancel "containing" and substitute -- in a form suitable for flame spraying formed of --

Claim 32, line 2, after "a" insert --metal--

line 3, cancel "material" and substitute --metal --.

Claim 33, line 2, after "a" insert --metal -- line 3, cancel "material" and substitute --metal --.

Claim 34, line 2, after "a" insert -- metal -- line 3, cancel "material" and substitute -- metal --.

Claim 35, line 2, cancel "components" and substitute --metal nucleus and metal differing from said nucleus --.

Claim 36, line 2, after "divided" insert -- metal --.

Claim 40, lines 1 and 2, cancel "suitable for use in the process of claim 1", line 2, after "separate" insert --metal --.

Claim 41, lines 1 and 2, cancel "suitable for use in the process of claim 1", line 2, after "separate" insert --metal --.

Claim 42, lines 1 and 2, cancel "suitable for use in the process of claim 1", line 2, after "separate" insert --metal --.

Claim 43, lines 1 and 2, cancel "suitable for use in the process of claim 1", line 2, after "separate" insert --metal --.

Claim 44, lines 1 and 2, cancel "suitable for use in the process of claim 1", line 2, after "first" insert --metal -- line 3, after "second" insert --metal --.

Claim 46, lines 1 and 2, cancel "suitable for use in the process of claim 1", line 3, after "separate" insert --metal --.

Claim 52, lines 1 and 2, cancel "suitable for use in the process of claim 1", line 2, cancel "containing" and substitute -- in a form suitable for flame spraying formed of --, line 3, after "two" insert -- metal --.

REMARKS

The Official Draftsman has been requested to correct the drawing by providing the required border line.

The claims have been amended in an endeavor to overcome the Examiner's formal objection thereto as set forth in the third paragraph of the Action.

The designation of the metal components in terms of their capability of exothermically reacting by forming an intermetallic compound is not believed functionally objectionable. The entire point of novelty is the formation of the plate spray composite with the specific selection of components which are reactive in this manner. Materials which will exothermically react forming an intermetallic compound are well known in the art and within its broadest aspects the invention includes the selection of any two such metals. The applicants have pointed out in the specification that any metal combinations which are capable of reacting in this manner are useful in accordance with the invention and have given working examples of almost 200 such combinations. A consideration of the principal involved in the invention in combination with this broad disclosure and large number of supporting working examples should entitle the applicants to the broad claimed terminology. The Examiner is questioned as to what metal combinations he believes are included within the scope of the claim which are not supported by the specification and which would not be expected to be operable from the standpoint of exothermically reacting together to form the intermetallic. The relative proportions of the components are not critical and it is merely necessary that the same are capable

compound. Proportions which will not so react are, of course, not included within the scope and terminology of the claims.

The Examiner's objections to the phrase "listed in Table 1" as indefinite is questioned. Table 1 lists many specific pairs of metal components and it is not seen what can be indefinite with respect to this clear and concise listing. The reference to Table 1 in the claims is identical as if the table itself were listed and incorporated in the claim. When considering the length of Table 1, the practicality of incorporation by reference rather than repetition can well be appreciated.

The applicants' invention as set forth in the instant application is believed to be directed to a major breakthrough and pioneering development in the flame spray field. Flame spray, of course, is a relatively old art going back to the turn of the century. For a satisfactory flame spraying process it is necessary that the sprayed coating bond or adhere to the base or substrated being sprayed. In order to obtain a satisfactory bonding it has generally been considered necessary to physically roughen the surface being sprayed to such a degree that actual undercuts or cavities are formed into which the sprayed metal particles key and lock. The physical roughening was generally effected by a severe grit blast roughening or a mechanical machine roughening, or in accordance with one procedure by means of knurling stippling. This surface preparation treatment was universally followed in the flame spraying field until the discovery by a Mr. Shepard (one of the coinventors herein) that molybdenum had the unique property of being able to bond to a clean surface without this surface preparation (see U.S. Patent 2 [illegible]).

For some reason the molybdenum would adhere to a clean unprepared surface with a tenacious bond and further flame spray coatings could be applied thereover so that the molybdenum could be used as a bonding coat or treatment. With the advent of this discovery by Mr. Shepard the spraying of the molybdenum bonding coat became an extremely wide spread and preferred bonding treatment in the art. Due to this characteristic of the molybdenum of being able to bond to the surface without the conventional surface preparation the molybdenum became known as a "self-bonding" flame spray material.

From the very beginning of the flame spray art considerable endeavors were made to improve the bonding of the sprayed material to the base and to develop materials and/or processes which would allow bonding without the conventional surface roughening. Since the discovery of Mr. Shepard that molybdenum was self-bonding constant and extensive research efforts were directed to the finding further self-bonding materials. In spite of these extensive efforts and the long felt need in the art no one was successful in developing a further satisfactory self-bonding material until the advent of the instant invention.

The applicants in accordance with the invention have surprisingly and unexpectedly discovered that if the flame spray material is in the form of a composite containing the two metal components which are capable of exothermically reacting together with the formation of an intermetallic compound, the material is self-bonding when flame sprayed. Furthermore the coating formed is generally a superior coating and in most cases has a higher melting point and is thus more resistant than the components. In connection with this higher melting point the in-

vention furthermore affords the advantage of allowing the flame spraying of a higher melting point coating at a lower spraying temperature.

The applicants' invention has met with immediate commercial success and materials, i.e. both powder and wire produced in accordance therewith are being marketed not only as a substitute for molybdenum, but as a material for producing novel high grade coatings with unique characteristics.

In order to achieve the effect in accordance with the invention the flame spray material cannot be in the form of a mere mixture, but must be in the form of a composite containing the components physically bound together in contact, i.e. in the form of a wire or a powder the individual granules of which contain the components physically bound together. Thus, for example, where the powder contains nickel and aluminum, each granule must contain portions of nickel and aluminum bound together and a mere mixture of nickel powder and aluminum powder will not be operative.

While it is appreciated that due to the requirements for restriction the claims being prosecuted are limited to a material, nevertheless, in considering obviousness under 35 U.S.C. [illegible], the invention as a whole must be considered and unique and [illegible] properties which a material possesses must be considered in determining whether the claimed invention would be obvious from the art cited. [In re Papesch, 137 USPQ 43, 50 CCPA [illegible]]

A characteristic of the claimed flame spray material in accordance with the invention is its ability to exothermically form the intermetallic compound in situ during spraying which gives it the unique characteristic of a self-bonding mater-

It is submitted that such a material would not be obvious under 35 U.S.C. 103 from the art cited by the Examiner and that none of the cited reference either singly or [illegible] disclose a material having this unique characteristic, or a material which could be used for the same purpose as the material claimed herein. Furthermore, there is nothing in the cited art which would teach a material equivalent to the claimed material.

The basic reference is the patent to Bayer which relates to the formation of a refractory coating on metals with the use of a Thermit-type reaction, i.e. an oxidation reduction. In accordance with the Bayer disclosure a coating layer containing a metal such as aluminum and an oxide such as iron oxide is formed involving the oxidation of the initial metal and reduction of the oxide forming the refractory coating. In accordance with one embodiment a mixture of the metal and metal oxide, i.e. the Thermit mixture is sprayed on a base heated to a sufficient temperature to allow Thermit reaction to occur after the [illegible] particles deposit. Thermit materials and other materials which exothermically react by an oxidation reaction are of course, been known for many years and have never proven useful for commercially successful in flame spraying. Such materials normally do not produce satisfactory as-sprayed coatings and are [illegible] bonding. In this connection it should be noted that in accordance with Bayer the spraying must be effected on a base which is preheated to an extremely high temperature and the reaction only occurs after the deposit of the particles on this hot [illegible]. One of the advantages of the flare spray process is that it does not require a heating of the base and the coating can be [illegible]

with the base remaining relatively cool. There is nothing in the Bayer patent which teaches a composite as claimed and required by the applicants, and at best there is a teaching of a powder mixture, i.e. the Thermit mixture. Thus, even following the rationale used by the Examiner in rejecting the claims and substituting nickel and aluminum for the metal oxide-metal Thermit mixture, there would merely result a mixture of aluminum and nickel powder which, of course, has nothing to do with the applicants' claimed invention and is not the equivalent thereof. Still further, the whole purpose of the Bayer teaching is the formation of a refractory coating and thus it would not be proper to substitute materials which do not contain oxygen for Bayer's Thermit materials.

Turning to the secondary references per se, the Schrewelius patent simply relates to a flame spray mixture containing a metal component and a separate boron component, the purpose of the boron component being to flux or reduce the oxide film formed on the surface of the metal particles. While intermetallic compounds are mentioned, these are preformed intermetallic compounds utilized as the metal component. There is thus nothing in Schrewelius which has any relation to the applicants' basic inventive concept and apparently the references has been solely cited to show the use of boron in flame spray powders, presumably pertinent with respect to claim 51. With respect to this claim, however, the applicants are relying on the basic concept of the composite containing exothermically reacting intermetallic compound forming components and are only claiming this in combination with the fluxing element. The applicants readily admit that the use of fluxing elements in flame spraying and more specifically in oxy-weld processes is well known in the art.

Grala et al has been cited to show that nickel and aluminum will exothermically react to form an intermetallic compound. The applicants readily admit that this was well known in the art, as was the fact that other specific metal pairs would also react in this manner. The applicants do not claim this known phenomena as their invention is limited to the concept of combining the metals which are known to react in this manner into the flame spray composite which produces the completely novel flame spray material. There is, of course, nothing in the prior art which would teach or indicate that merely because components would react in this manner that they would be useful as flame spray material or that the same should be combined in a specific form in order to make a successful self-bonding flame spray material.

The Examiner has cited the Herz reference as showing that it is old and well known to have powdered metals for flame spraying in hydride form. As Herz primarily relates to powder metallurgy and not to flame spraying, it is assumed that this reference has actually been cited to show that the hydride may be used in place of the metal in intermetallic compound formation. Actually the Herz disclosure is limited to the teaching of the use of zirconium hydride powder in forming a sintered Ni-Al-Zr composition. The question as to whether it would be obvious to use the metal in the form of a hydride, or include a hydride in the applicants' invention need not be considered as the very basic concept of the flame spray composite containing the reactive components is nowhere taught in the prior art.

The Mackiw patent has been cited to show coated powder which is used in powder metallurgy. None of the coating-

Nucleus combinations disclosed by Mackiw are exothermically reactive to form an intermetallic compound and there is nothing in the art which would suggest the substitution of such a combination for the combinations taught by Mackiw. Furthermore, Mackiw's coated powders are not the equivalent of those claimed by the applicants and do not have the unexpected characteristics of the applicants' claimed powders. Conversely, there is no basis for substitution of coated powders for Bayer's mixture and even if Bayer's mixture were made into a composite, the same would merely be a Thermit composite and have no relation to the applicants' claimed invention.

In summary, it is again emphasized that there is not the remotest suggestion in any of the references or any combination thereof, of a flame spray material in the form of a composite containing the two metals which are capable of exothermically reacting to form an intermetallic compound. This inventive concept of the applicants has provided a major breakthrough in the flame spray field and most certainly constitutes an invention which is not obvious from the prior art and which is meritorious of patent protection.

In view of the above, reconsideration and allowance of the claims is hereby solicited.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By: _____
Attorneys for Applicants

E 678

IN THE UNITED STATES PATENT OFFICE

Applicant : Ferdinand J. Dittrich et al

Serial No. : 442 727 Group 110

Filed : March 25, 1965

For : FLAME SPRAYING EXOTHERMICALLY REACTIVE INTERMETALLIC COMPOUND FORMING COMPOSITES

May 24, 1966

Hon. Commissioner of Patents
Washington, D. C.

RECEIVED
JUN - 1 1966
GROUP 110

ATT: OFFICIAL DRAFTSMAN

Sir:

Kindly amend the drawing in the above application by providing the border line as required.

Kindly charge the same to the account of the [illegible] account No. 02-4740.

Respectfully submitted,

BUFFALO, NIAGARA & [illegible]

By: [signature]
Attorney

CORRECTED
NOV 28 1966
APPROVED
FILED

ADDRESS ONLY THE COMMISSIONER OF PATENTS WASHINGTON, D.C. 20231

Paper No. 9

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

E 680

Burgess, Dinklage and Sprung
605 Third Avenue
New York, New York 10016

In Reply Please Refer to The Following: 111

Applicant: Ferdinand J. Dittrich et al.

Ser. No.: 442,727

Filed: March 25, 1965

For: FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

SHORTENED TIME FOR REPLY

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

Responsive to the amendment filed May 27, 1966.

Claims 26-46 and 49-55 are rejected under 35 U.S.C. 103 as unpatentable over Bayer in view of Schrewelius, Herz, Grala et al., and Mackiw et al. for the reasons set out in Paper No. 6.5.

The applicants state that their entire point of novelty is the formation of the flame spray composite with the specific selection of components which are exothermically reactive. Page 3, lines 10-12 of the amendment. The applicants further argue that unique and unexpected properties which a material possesses must be considered in determining whether the claimed invention would be obvious from the art cited. The Mackiw et al. reference teaches that it is old to form composites of metal powders by having a metal coating covering a metal nucleus. The metals can be nickel and aluminum. The Grala et al. reference teaches that nickel and aluminum are exothermically reacting elements. Also, it is pointed out that metals which will exothermically react to form intermetallic compounds are well known in the art, as the applicants admit on page 3, lines 12-15 of the amendment. Therefore, since it is well known that certain

metals will exothermically react to form intermetallic compounds what unique and unexpected properties does the claimed material posses that would make it unobvious from the art cited? See page 6, lines 18-24 of the amendment. Since the applicants state that the entire point of novelty is the formation of the composite with the specific selection of components which are exothermically reactive it is held that the claimed material possesses no new and unobvious properties that the prior art does not expect. The applicants main arguments are concerned with the use to which the material is to be put. But finding a new use for an old material is not a basis for claiming the material. In re Thuau, 554 O.G. 14, 1943 C.D. 390. Also, indications of the field of contemplated use in the preamble is not a limitation to be considered in the question of patentability. In re Hack, 1957 C.D. 334, 721 O.G. 422.

Claims 1-25, 47 and 48 are withdrawn from further consideration by the Examiner, Rule 142(b), as being for a nonelected invention, the requirement having been traversed in Paper No. 6.

No claim is allowed.

This action is made FINAL.

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS ACTION IS SET TO EXPIRE THREE MONTHS FROM THE DATE OF THIS LETTER.

ROD

RODean:mjs

WO 7-3621

David L. Recb

DAVID L. RECK

EXAMINER

NOV 14 1966 U.S. PATENT OFFICE

E 682

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al

Serial No. : 442 727

Filed : March 25, 1965

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

November 9, 1966

Hon. Commissioner of Patents
Washington, D. C.

Sir:

The following is in response to the Office Action dated September 23, 1966. Kindly enter the following amendment:

Claims 26, 27, 28, 29, 32, 33, 34, 37, 38, 40, 42, 43, 44, 46, and 52, last line of each claim, after the word, add the following and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

REMARKS

Reference is made to the conference most courteously extended by the Examiner, at which the applicants' invention contribution were discussed in detail and during which certain technical brochures and promotional material issued by the applicant with reference to the presently commercially available embodiments of the invention were presented to the Examiner.

As discussed at the conference, none of the references disclose a composite powder or other composite suitable for flame spraying formed of the two required components which are capable of exothermically reacting with each other forming an inter-

82

metallic compound. The Mackiw et al reference mention of aluminum and nickel is merely a mention of these components in large lists of compounds with no teaching or indication of the selection of these individual components from these lists, or that any advantage could be gained by the selection of these specific components as compared to the extremely large number of choices available.

As further discussed, the rejection of the claims is not under 35 U.S.C. 102, but is under 35 U.S.C. 103. In determining obviousness under 35 U.S.C. 103 the unexpected properties which the material possesses must be considered. In this respect it was agreed that the unexpected properties are the unexpected properties which the material would show when flame sprayed, i.e. the unexpected properties which the material possessed as a flame spray powder and not simply the properties of being capable of exothermically reacting. These unexpected properties are not obvious from the prior art.

The claims have been amended in the manner agreed upon at the conference and it is thus believed that the above in accordance with the conference places the application in condition for allowance, which is hereby solicited.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By: _____
Attorneys for Applicants

NOV 14 1966 U.S. PATENT OFFICE

E 684

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al

Serial No. : 442 727 Group 111

Filed : March 25, 1965

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

November 10, 1966

Hon. Commissioner of Patents
Washington, D. C.

Sir:

Supplemental to the Amendment dated November 9, 1966, kindly cancel claims 1-25, 47 and 48 without prejudice.

REMARKS

The claims directed to the non-elected invention have been cancelled without prejudice in order to facilitate prosecution and place the application in condition for allowance.

Respectfully submitted,

BURGESS, DINKLAGE & [illegible]

By [signature]
Attorneys for [illegible]

E 685

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON, D.C. 20231

Paper No. 12/7

In Reply Please Refer To:

Burgess, Dinklage and Sprung
605 Third Avenue
New York, N. Y. 10016

Applicant	Ferdinand J. Dittrich, et al.
Ser. No.	442,727
Filed	Mar. 25, 1965
For	FLAME SPRAYING EXOTHERMICALLY REACTIVE INTERMETALLIC COMPOUND FORMING COMPOSITES

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

EXAMINER'S CHANGE AND/OR ADDITION TO THE APPLICATION RECORD UPON ALLOWANCE

This application is in condition for allowance. Changes and/or citation of references are specified below. Should this not be acceptable to applicant, an appropriate amendment may be proposed under Rule 312. To ensure consideration of such amendment, it should be submitted on or before the date of remitting the issue fee.

PROSECUTION ON THE MERITS IS CLOSED AND A NOTICE OF ALLOWANCE WILL BE MAILED IN DUE COURSE.

The changes and/or additions are as follows:

Page 1 line 2, the words ",now abandoned" have been inserted after "1960".

Page 1, line 4, the words ", now abandoned" have been inserted after "1962".

Hyland Bizot
HYLAND BIZOT
EXAMINER

RoD
RODean:lb
WO 7-3621
11/28/66

Form PO-55
12-64

E 686

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE

PAPER NO.: 13

SERIAL NO.: 443,727

REFERENCES CITED BY EXAMINER

The following references, cited by the examiner, are of record in the patented file of this patent:

UNITED STATES PATENTS

PATENT NUMBER	DATE	NAME OF PATENTEE	OFFICIAL CLASSIFICATION
1,379,063	5/1921	Van Allen	29-191
2,853,403	9/1958	Mackiw et al.	117-100
2,884,688	5/1959	Hers	75-170
2,910,356	10/1959	Grala et al.	75-170
2,933,415	4/1961	Homer	29-191
3,0[illegible]182	3/1962	Schrewelius	117-105
3,0[illegible]409	8/1962	Bayer	117-22
3,121,643	2/1964	Eisenberg	117-105.2
3,135,626	6/1964	Moon et al.	117-105.2

FOREIGN PATENTS

PATENT NUMBER	DATE	COUNTRY

OTHER REFERENCES

(List the following items when available, page number, date, and title)

E 687

Form PO-611
(12-64)

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

EXAMINER(S) NAMED IN ALLOWED ACTION

The examiners with full or partial signatures appear upon the action in the case are named below. The examiner shall sign on the printed copies of the patent, and the final matter thereon.

[illegible]	
RICHARD D. LeVIUS	
[illegible]	
A. GOLIAN	
R. O. [illegible]	

POL-85
(6-64)

E 688

ADDRESS ONLY
THE COMMISSIONER OF PATENTS
WASHINGTON, D. C. 20231

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications regarding this application should give serial number, name of art unit and name of the applicant.

NOTICE OF ALLOWANCE AND ISSUE FEE DUE

The application for patent identified below has been examined and found allowable for issuance of Letters Patent.

	FILING DATE	SERIAL NO.	NO. OF CLAIMS ALLOWED	EXAMINER
	01/23/65	442727	28	Rask
APPLICANT	Dittrich, Ferdinand J.; Bellmore, L. I., and Shepard, Arthur P.; Flushing, L. I., N. Y.			MAILED Jan. 12, 1967
TITLE OF INVENTION (If written as amended by examiner)	Flame spraying exothermically reacting intermetallic compound forming composites			
	NO. SHEETS @ $2 EACH	NO. PAGES @ $10 EACH	ISSUE FEE DUE	CLASS-SUB
	001	11	$212	029/191.2

With the allowance of the application, the above indicated Issue Fee becomes due and payment must be made within three months of the date of this Notice or the application shall be regarded as abandoned.

The Issue Fee is one hundred dollars ($100) plus two dollars ($2) for each printed sheet of drawing and ten dollars ($10) for each printed page of specification, or portion thereof.

Inasmuch as the number of printed pages of specification must be determined in advance of printing from the amount of matter in the allowed application, the Issue Fee is subject to change. After the patent has been printed, the estimate will be reviewed in light of the actual number of pages of specification. If it is found that an overcharge is made, you will be notified thereof with the issuance of the Patent and the matter will be referred to the Finance Branch for appropriate action. If the number of pages is underestimated by two or more pages, you will receive a notice of Additional Issue Fee Due with the Patent and payment of this amount must be made within three months of the date of that Notice. Failure to remit any additional fee due within three months from the date of that Notice will result in lapse of the Patent.

As a convenience in remitting this fee, use of the enclosed Form POL-85a is suggested. The Issue Fee will not be received from anyone other than the applicant, his assignee or attorney, or a party in interest as shown by the records of the Patent Office. A form is enclosed relating to the address of the inventor's choice, to which your attention.

If it is desired to have the patent issued to an assignee or assignees, an assignment, together with the fee for recording the same, must be filed in this Office on or before the date of payment of the Issue Fee.

The patent will be issued and forwarded within approximately two months after receipt of the Issue Fee.

By direction of the Commissioner.

Burgess, Dinklage, et al
605 Third Ave.
New York, N. Y. 10016

77

E 689

APR 6 1967 U.S. PATENT OFFICE

PATENT OFFICE APR 12 1967

IN THE UNITED STATES PATENT OFFICE

Applicants: Ferdinand J. Dittrich et al.

Serial No.: 442,727

Filed: March 25, 1965 Group 110

For: FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

SUPPLEMENTAL DECLARATION

We, the undersigned, declare with respect to the above-entitled application that the subject matter of the allowed claims was part of our invention, was invented before we filed our original application, above-identified, for such invention; that we do not know and do not believe that the same was ever known or used before our invention thereof, or patented or described in any printed publication in any country before our invention thereof, or more than one year before our application, or in public use or on sale in the United States more than one year before the date of our application, that said invention has not been patented in any foreign country before the date of our application on an application filed by us or our legal representatives or assigns more than 12 months prior to our application in the United States, and has not been abandoned.

The undersigned petitioners declare further that all statements made herein of their own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 3/13/67 Inventor: Ferdinand J. Dittrich (Signature)
Ferdinand J. Dittrich (Typed name)

Date: 3/3/67 Inventor: Arthur P. Shepard (Signature)
Arthur P. Shepard (Typed name)

Date: _____ Inventor: _____ (Signature)
(Typed name)

Date: _____ Inventor: _____ (Signature)
(Typed name)

E 690

POL-85a (6-66)

Metco 305

U.S. [illegible] Patent Office

ISSUE FEE TRANSMITTAL

This form is provided for [illegible] transmitting Issue Fees to the Patent Office. When properly completed it may be used in lieu of a formal transmittal [illegible] will note and list in items numbered 1 thru 5 below. The Issue Fee Data printed [illegible] will be mailed to the address [illegible] or upper left of this form. If desired, use the reverse side of [illegible] for a receipt copy when complet[illegible]

1. The COMMISSIONER [illegible] requested to apply the enclosed issue fee to the application identified below, and deliver the patent as indicated.

BURGESS, DINKLAGE & SHEPP

April 5, 1967
Date

By [illegible]

NOTE – Issue Fees will not be received from other than the applicant, his assignee, or attorney, or a party [illegible] interest as shown by the records of the Patent Office. Issue Fees will not be applied to pending applications.

	FILING DATE	SERIAL NO.	NO OF CLAIMS ALLOWED	GRP A.U.
	03/23/65	442727	20	Rec'd 11-
APPLICANT	Dittrich, Ferdinand J.; Bellmore, L. I., and Shepard, Arthur P.; Flushing, L. I., N. Y.			Mailed Jun. 12, 1967
TITLE OF INVENTION (If not correctly as printed by examiner)	Flame spraying exothermically reacting intermetallic compound forming compositions			
	NO. SHEETS OF DR. EACH	NO. PAGES OF SPEC. EACH	ISSUE FEE DUE	CLASS-SUB
	001	11	$21[illegible]	[illegible]

2. Assignee

METCO INC.

CREDIT APPLIED

CODE(S) 10[illegible] 220[illegible]

[illegible]

[illegible]

MAY 2 2 1967 BY: [illegible]

3. FEE ENCLOSED

APR 1 9 1967

As of [illegible] fee(s) were credited

$[illegible].00

Fee Code(s) 106 107 [illegible]

[illegible]

MAILING INSTRUCTIONS

NOTE – The office will send the patent to the address entered in stub or left below unless you direct otherwise. Use the spaces provided to indicate any changes which affect the delivery of the patent. However, if an additional Issue Fee Due Notice is required this action is cancelled and the patent will be mailed to the address entered in the stub or left below.

4. Do not send the patent to the addressee listed below. Send patent to (check one)

☐ Patentee

☐ Assignee

☐ Associate Attorney (See specific authorization in file)

☐ Change of address – Attorney [illegible]

The address of the person checked above is typed in Item 5 below.

[illegible]

BY [illegible]

5. (If an additional Issue Fee is required the patent will not be sent to this address – PLEASE FURNISH ZIP CODE)

90

E 691

BURGESS, DINKLAGE & SPRUNG
Attorneys at Law
605 Third Avenue
New York, N.Y. 10016

Date: April 5, 1967

ON ALL PAPERS PLEASE FURNISH OUR

FILE NO. [illegible]

Hon. Commissioner of Patents
Washington, D.C. 20231

Serial No. : [illegible]
Filed : 3/[illegible]
Group : 110

Dear Sir:

Re the application of FERDINAND J. DITTRICH, et al

for FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

we enclose

( ) Specification

( ) Declaration, Power of Attorney and Petition

( ) _____ Sheet(s) Drawings

( ) $ .00 filing fee (to be charged to Account No. 02-4740).

(x) $ 212.00 issue fee (to be charged to Account No. 02-4740)

( ) Assignment and $20.00 recording fee (to be charged to Account No. 02-4740)

(x) Supplemental Declaration

( ) Priority is hereby claimed on the basis of the following:

Country	Serial No.	Date

Basic fee.....$[illegible]
_____ claims over 10 at $2..... $
_____ independent claims over 1 at $10.... $____

Respectfully,
BURGESS, DINKLAGE & SPRUNG

By [signature]

91

E 692

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON, D.C. 20231

Paper No. 10

In Reply Please Refer To: [illegible]

Burgess, Dinklage & Sprung
605 Third Avenue
New York, N. Y. 10016

Applicant: [illegible]	
Ser. No. [illegible]	MAILED
Filed [illegible]	[illegible]
For [illegible]	[illegible]

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

EXAMINER'S CHANGE AND/OR ADDITION TO THE APPLICATION RECORD UPON ALLOWANCE

This application is in condition for allowance. Changes and/or citation of references are specified below. Should this not be acceptable to applicant, an appropriate amendment may be proposed under Rule 312. To ensure consideration of such amendment, it should be submitted on or before the date of remitting the issue fee.

PROSECUTION ON THE MERITS IS CLOSED AND A NOTICE OF ALLOWANCE WILL BE MAILED IN DUE COURSE.

The changes and/or additions are as follows:

In the specification: page 9, line 6, the phrase "marked 1" has been cancelled, also in line 7, the phrase "marked 2" has been cancelled.

The above cancellations were authorized by Mr. Arnold Sprung, the applicants' attorney on May 8, 1967 in a telephone interview.

[illegible]
EXAMINER
[illegible]

RCLean:tmp
W07-3621

E 693

Form PGL 307
(6-66)

PATENT ISSUE FEE NOTICE OF OVERPAYMENT

[ ]

[ ]

Review of the printed pages of the above identified patent indicates the following issue fee overpayment:

ISSUE FEE	AMOUNT
[X] PRINTED PAGES OF SPECIFICATION	$ 20.00
[ ] PRINTED PAGES OF DRAWING	$
[ ] BASIC ISSUE FEE	$
Total if more than one fee	$

This matter has been referred to the Finance Branch for appropriate action.

By Direction of the Commissioner of Patents

PLEASE FURNISH YOUR ZIP CODE IN ALL CORRESPONDENCE - IT IS AN ESSENTIAL PART OF YOUR ADDRESS

93

E 694

IN THE UNITED STATES PATENT OFFICE

Applicants : Ferdinand J. Dittrich et al.

Serial No. : 442,727

Filed : March 25, 1965 Group

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Patent No. 3,322,515 Issued May 30, 1967

June 12, 1967

Hon. Commissioner of Patents
Washington, D.C.

Application for Certificate of Correction

Sir:

Applicants and their assignee of the above entitled application and patent issued thereon respectfully show as follows:

I. The above application issued to Patent No. 3,322,515 on May 30, 1967.

II. Column 3, line 49 (specification, page 7, line 14) cancel "the" before "grams"

III. Column 7, line 5 (specification, page 16, line 14) "as a pressure" should be --at a pressure--

IV. Column 7, line 12 (specification, page 16, line 21) correct the spelling of "deposit"

V. Column 7, line 69 (specification, page 19, line 6) "aluminum" should be --alumina--

VI. Column 9, line 6 (specification, page 22, line 14) "sprayer" should be --sprayed--

line 75

VII. Column 16, last line, correct the spelling of "reacting"

VIII. The mistakes hereinabove complained of were incurred through the fault of the Patent Office and without any fault whatsoever on the part of the said applicants or their assignee, as clearly disclosed by the files or records of the Patent Office.

IX The original deed of the said patent is herewith returned.

WHEREFORE the said applicants and their assignee pray that a Certificate of Correction duly issue and be endorsed upon said Letters Patent and recorded in the records of patents, stating the fact and nature of said mistakes herein complained of, and that a printed copy of such Certificate be attached to each printed copy of the specification.

Respectfully submitted,

BURGESS, DINKLAGE & STURM

BY _____

Attorneys for Applicants and their Assignee

E 696

INDEX OF CLAIMS

Claim No.	Original	Date			Claim No.	Original	Date		
		2-6	9-14-66	11-23-66					

SEARCHED

Claim	Sub	Date	Ex'r
117	105 105.2 146 100 93 22	3/21/66	ROB
29	191 191.2 191.6 192 194 195		
95	95 170 171		
106	1		
	Update	Date 9/14/66	ROB
Update Date		11/23/66	ROB

INTERFERENCE SEARCHED

Claim	Sub	Date	Ex'r
117	105 105.2 146 100 93 22	11/23/66	ROB
29	191 191.2 191.6 192 194 195		
95	95 170 171		
106	1		

STATUS

96

3,270,797

10-4-65

E 697

CLASSIFIED GROUP 1

CONTENTS

1.	Application papers. Print	26.	
2.	Reg for Ref Apr. 9 1965	27.	
3.	Amendment May 13, 1965	28.	
4.	Amendment July 13, 1965	29.	
5.	RESTRICTION (SSP) OCT 22 1965	30.	2 - sheets
6.	Letter Nov. 16, 1965	31.	
7.	Reject for (3 mos) Apr. 5, 1966	32.	
8.	Amdt. May 27, 1966	33.	
9.	Letter to Aft. May 27, 1966	34.	
10.	FINAL REJECTION 3 mos. SEP 28	35.	
11.	Amdt. A (R.E.) Nov. 14, 1966	36.	
12.	Amdt. B (R.E.) Nov. 14, 1966	37.	
13.	[illegible] 17 NOV 28 1966	38.	
14.	LIST OF REFERENCES List of Exrs. Names	39.	
15.	Supp. Resp. Apl. 6, 1967	40.	
16.	Ex. Cert.	41.	
17.	Req for C of C 6-13-67	42.	
18.		43.	
19.		44.	
20.		45.	
21.		46.	
22.		47.	
23.		48.	
24.		49.	
25.		50.	

E 698

592238

Class 117 Subclass 105.1

Filed complete (Date) MAY 26, 1966 Serial No. 592 238

(36)

Applicant(s)

DITTRICH, FERDINAND J. OF BELLMORE, N.Y. AND SHEPARD, HERB P. OF FLUSHING, N.Y.

Assignee Metco, Inc., a Corp. of New York

Title of Invention

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Division of Continuation Continuation-in-part Reissue

Total claims 27 Ind. claims 3 Filing fee rec. $119 Transaction Atty's docket METCO 305.9

Serial No. 473,777 Filed

New Patent No. 3,323,878

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PARTS OF APPLICATION FILED SEPARATELY

E 699

1737-205

CONTENTS

1. Application & other papers.
2. 1st Amdt A Mar. 31, 1967
3. REJECTED (3) Dec 14, 1967
4. Amdt C Jan 16, 1968
5. Final Rej (5th) FEB 13 1968
6. Req. for 1st Time
7. Request Granted
8. Req for 2nd time
9. Amdt D
10. Amdt C (Rec'd)
11. Ref 255
12. Ltr vo. Amdt E
13. Ltr of Abp.
14. Affidavit
15. Amdt F
16. [redacted] 875
17. Amdt F (R-312)
18. Notice of Entry (312)
19. Amdt (I)
20. Supplemental Declaration 1-23-68
21. Req for Abp
22. Abandoned Dec. 1, 1969
23.
24.
25.
26.
27.

875 05

APPEAL NO.

DOWNGRADED AT 3 YEAR INTERVALS; NOT AUTOMATICALLY DECLASSIFIED

E 700 . INDEX OF CLASSES

SEARCHED

Class	Sub	Date	Exr

Class	Sub	Date	Exr

MAY 26 1966 U.S. PATENT OFFICE

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E 701

5922[illegible]

As of MAY 31 1966 fee(s) were applied to

Fee Code(s) 101 $65.00 [illegible] May 25, 1966

Patent Office

102 $54.00 (Authorized Signature)

Hon. Commissioner of Patents
Washington, D. C. 20231

Re: Our File Metco 305.5

Sir:

In accordance with Rule 147 applicants wish to file a divisional application of:

Applicant S.N.	:	442 727
Applicants	:	Ferdinand J. Dittrich and Arthur F. Shepard
Filed	:	March 25, 1965
For	:	FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES.

The divisional application is to be directed to claims 1 to 25, 47 and 48 in connection with which restriction has been required.

The Office is requested to prepare certified copy of application S.N. 442 727 filed March 25, 1965, to serve as application papers and to charge the same to the account of the undersigned, account No. 02-4740.

The Office is also requested to charge the filing fee of $110.00 to the account of the undersigned, account No. 02-4740.

Respectfully,

BURGESS, DINKLAGE & SPRUNG

By: [signature]

AS/k

E 702

U. S. DEPARTMENT OF COMMERCE
UNITED STATES PATENT OFFICE

November 7, 1966
(Date)

THIS IS TO CERTIFY that the annexed is a true copy from the records of this office of the Application of Ferdinand J. Dittrich and Arthur P. Shepard, as originally filed March 25, 1965, Serial Number 442,727, for Flame Spraying Exothermically Reacting Intermetallic Compound Forming Composites.

Ribbon cut in Application Branch

By authority of the
COMMISSIONER OF PATENTS

Certifying Officer.

E 703

MAY 26 '66

APPLICATION DIV.
U.S. PATENT OFFICE

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

COPY DELIVERED

This is a continuation-in-part of copending applications, Serial No. 72,343 filed November 2, 1960, now abandoned, issued as U.S. Patent 3,254,970, Serial No. 134,544 filed August 16, 1961, Serial No. 231,786 filed October 26, 1962, now abandoned, and Serial No. 343,705, filed February 10, 1964, now abandoned.

This invention relates to the flame spraying of exothermically reacting intermetallic compound forming composites. The invention more particularly relates to the flame spraying of flame spray materials in the form of composites containing two or more components which will exothermically react with each other during the spraying, forming one or more intermetallic compounds, and to a novel group of such composites including powders and wires.

Flame spraying involves the feeding of a heat-fusible material into a heating zone, wherein the same is melted or at least heat-softened, and then propelled from the heating zone in a finely divided form, generally onto a surface to be coated.

The material being sprayed is generally fed into the heating zone in the form of either a powder or a wire (the latter term designating both rods and wires). The spraying is effected in a device known as a heat-fusible material spray gun or a flame spray gun.

In the wire type flame spray gun the rod or wire of the material to be sprayed is fed into the heating zone

formed by a flame of some type, where it is melted or at least heat-softened and atomized, usually by blast gas, and thence propelled in finely divided form onto the surface to be coated. The rod or wire may be a conventionally formed rod or wire of a metal, or may be formed by sintering together finely divided material, or by bonding together finely divided material by means of a plastic binder or other suitable binder which disintegrates in the heat of the heating zone, thereby releasing the material to be sprayed in finely divided form.

For spraying finely divided, i.e., powdered material, a powder type flame spray gun is used in which the powder, usually entrained in a carrier gas, is fed into the heating zone of the gun formed by a flame of some type. The powder is either melted or at least the surface of the grains heat-softened in this zone, and the thus thermally conditioned particles propelled onto a surface to provide a coating. In the powder type spray gun as no "atomizing" energy is required, a separate blast gas is often dispensed with, though the same may be supplied in order to aid in accelerating the particles and propelling them toward the surface to be coated.

The blast gas may be provided for both the wire type and powder type guns to perform the additional function of cooling the workpiece and the coating being formed thereon.

The heat for the heating zone is most commonly

produced from a flame caused by the combustion of a fuel, such as acetylene, propane, natural gas, or the like, using oxygen or air as the oxidizing agent. The heat may, however, also be produced by an electrical arc flame or, in the newer type of guns, by a plasma flame. The plasma flame may in itself constitute part of an electric arc, or, in accordance with a newer development, may be in the form of a "free plasma stream", i.e., a stream of plasma which may be considered independent of the arc as it does not contribute to the electric flow between electrodes.

Heat-fusible material spray guns utilizing electric resistance heating or induction heating as the heat source have also been proposed but have not proven commercially successful except in connection with the spraying of low melting point metals, such as solders, lead and zinc.

Flame spraying in the initial stages of its commercial development was used mostly for the spraying of various metals and was often referred to as metallizing. However, the art of flame spraying extends to the spraying of a much wider group of materials, including higher melting point or refractory metals, ceramics, cermets, and the like, and such materials are of increasing commercial interest.

In the case of spraying heat-fusible materials in the initial form of a rod or wire, the rod or wire is generally of a single composition, i.e., in the form of a specific metal, alloy, ceramic, or the like. While it is true that rods or wires formed from finely divided

material bound together with a binder of plastic or the like, as mentioned above, were known, the binder generally did not take part in the spraying or contribute to the coating, and merely served the purpose of maintaining the rod or wire in shape until fed into the heating zone.

In the case of flame spray powders, while powders formed of several constituents were known, the same were generally in the form of a powder mixture of the individual constituents or, at best, a particle aggregate.

One object of this invention is the spraying of the heat-fusible material in a novel form which allows the obtaining of superior results.

A further object of this invention is a novel group of flame spray materials.

These and still further objects will become apparent from the following description read in conjunction with the drawing in which:

Fig. 1 diagrammatically shows a cross-section of a grain of novel powder in accordance with the invention;

Fig. 2 is a cross-section of a further embodiment of an aggregate grain of novel flame spray powder in accordance with the invention;

Fig. 3 is a diagrammatic cross-section of an embodiment of a novel flame spray wire in accordance with the invention;

48

Fig. 4 shows a cross-section of a further embodiment of a novel flame spray wire in accordance with the invention; and

Fig. 5 shows a still further embodiment of a novel flame spray wire in accordance with the invention.

In accordance with the invention, the flame spraying is effected with the heat-fusible material in the form of a composite containing at least two components which will exothermically react with each other at the temperatures developed during the spraying, forming an intermetallic compound.

The term "composite" as used herein is intended to designate a structurally integral unit and does not include a mere mixture of components which may be physically separated without any destruction of the structure. Thus, in the case of powder, the term "composite" does not include a simple mixture of individual granules of the separate components, but requires that each of the individual granules contain the separate components which will exothermically react, forming intermetallic compounds. In the case of wire, the individual components must be incorporated in a single wire. In the composite the components must be in intimate contact with each other.

In connection with powders, each grain may consist of an aggregate containing the two components which will exothermically react, forming the intermetallic compound, but preferably the individual grains of the powder are in the form of a clad composite consisting of a nucleus of one of the components and at least one coating layer of the other component. Alternatively, the composite may consist

of separate, concentric coating layers of the two components and a nucleus of still a third material.

In the case of wires, the composites may be in the form of a wire having a coating sheath of one material and a core of the other, alternate coating sheaths of the componerts and a core of a third material, a wire formed by twising or rolling separate wire strands of the components, a wire consisting of a sheath of one component and a core containing the other component in powder or compacted form, a wire consisting of a sheath of one component and a core containing a compacted powder mixture of this same component material and one or more other components, a wire consisting of a plastic sheath and a core containing a compacted powder mixture of components, etc.

In order for the wires to be satisfactory for spraying, the same must not cavitate at the tip when heated, and should preferably be capable of forming a pointed or slightly tapered tip when being melted and sprayed. Thus, if the wires have an outer layer or sheath of one component and an inner core of another component, the inner core cannot have a lower melting point than the outer sheath, as otherwise the inner core will initially melt, causing cavitation at the tip. For example, if the wire is composed of nickel and aluminum as the exothermically reacting components and is in the form of a core with a coating sheath, the core must be nickel and the coating sheath aluminum,

as otherwise during the spraying the core will initially melt out, causing the cavitation which will interfere with a satisfactory spraying operation. The wire having the melting-point characteristics so as to allow the melting off of the tip without this cavitation, is referred to herein and in the claims as "non-cavitating wire."

As the components any two metallics which may be melted together to form an intermetallic compound in an exothermic reaction may be used. The components should release about 3000 calories per gram atom, and preferably at least 7500 calories per gram atom in the exothermic reaction forming the intermetallic compounds. The term "calories per gram atom" as used herein denotes the number of gram calories which the average atomic weight in grams of the intermetallic compound formed will generate in so being formed. While the components are preferably present in the stoichiometric proportions required for the formation of the intermetallic compound, it is, however, possible to also have an excess of one or the other provided the relative amounts are sufficient to release the quantities of heat indicated above in the formation of the intermetallic compounds.

An extremely large number of metal components are known which can be melted together in an exothermic reaction, forming an intermetallic compound with the generation of heat. Any of these component pairs may be utilized in accordance with the invention, it only being required

that the same be capable of being initially formed into the composite suitable for spraying and that the intermetallic compounds formed therefrom liberate the required amount of heat in the intermetallic compounds-formation and are suitable as components of a sprayed coating. As a general rule, components which will form intermetallic compounds having a higher melting point will liberate sufficient heat to be useful in accordance with the invention. In certain instances, however, components which will form intermetallic compounds which do not have as high a melting point, will also liberate sufficient heat in the exothermic reaction ... thus be useful. Preferred components are aluminum with at least one of Co, Cr, Mo, W, Ta, Nb, Ti, or most preferably Ni; or silicon with at least one of Ti, Nb, Cr, W, Co, Mo, Ni or Ta.

While iron itself is not a satisfactory component, the same may be present in addition to another component, which in itself is satisfactory, such as in the form of an alloy therewith. This other component, however, must be present in amount sufficient to form the intermetallic compound with the other component of the composite, with the generation of sufficient heat to aid the spraying operation. Thus, for example, iron which just contains enough alloyed nickel to render the same rust-resistant, does not contain enough nickel for an effective exothermic reaction with aluminum. Generally an alloy of nickel and iron must contain at least about 12% nickel for this purpose.

Fig. 1 shows a composite powder consisting of a nucleus of aluminum and a coating layer of nickel. Fig. 2

shows an aggregate of these components; and Figs. 3, 4, and 5 show various forms of wire containing these components; Fig. 3 showing a wire having an aluminum core with a nickel sheath, Fig. 4 showing a wire made of alternate strands of nickel and aluminum wire, as for example 18 strands of 25 gauge (.019" diameter) nickel wire marked 1, and 19 strands of 25 gauge aluminum wire marked 2; and Fig. 5 shows a sheath of aluminum filled with granules of nickel and aluminum.

Where one of the component metals is available as a metal hydride, the same may be used in this form rather than as a metal per se. When flame sprayed the hydrogen gas evolved from the hydride produces a reducing atmosphere, which in turn suppresses oxidation of the intermetallic compounds during and immediately after their formation. Thus, for example, in place of titanium, titanium hydride may be used as one of the components.

Also for the purpose of reducing oxidation a metal hydride, such as titanium hydride, may be added in a minor amount to the other components. Thus, for example, 1 $\frac{1}{N}$ 10% by weight, and preferably 1 $\frac{1}{N}$ 5% by weight, based on the total of the hydride and other components, may be used.

In addition, the powder granules and the wire may contain other conventional flame spray components, or be sprayed in admixture or in conjunction therewith. Thus, for example, the coated powders may additionally contain other coating layers of other flame spray components or may contain a nucleus of another flame spray material with

alternate coating layers of the components which will exothermically react, forming the intermetallic. In a similar manner, the aggregates or the wires may contain further flame spray components, and in the case of powders, the same may additionally be admixed with any other desired flame spray powder.

The clad powders, in accordance with the invention, may be formed in any known or desired manner, and preferably by the known chemical plating processes, in which coating material is deposited on a seed or nucleus of another material, or in which multiple layers of various materials are built up on the seed material, or in which various materials are co-deposited in a single layer on the seed material.

A mode of forming the clad powders involves the depositing of a metal from a solution by reduction on a seed or nucleus, such as by the hydrogen reduction of ammoniacal solutions of nickel and ammonium sulfate on a seed powder catalyzed by the addition of anthraquinone. It is also possible to form the coating by the use of other known coating processes, such as coating by vapor deposition, by the thermal decomposition of metal carbonyls, by hydrogen reduction of metal halide vapors, by thermal deposition of halides, hydrides, carbonyls, organo metals, or other volatile compounds, or by displacement gas plating and the like.

A preferred and greatly simplified mode of forming the clad powders in accordance with the invention

is the depositing of one component as a coating in the form of a paint on the other component. Thus, one of the components which is to form the coating or cladding, may be dispersed in finely divided form in a binder or lacquer so as, in effect, to form a paint in which this component corresponds to the pigment. The paint is then used to coat core particles of the other component and the binder or lacquer allowed to set or dry. The binder material is preferably a resin which does not depend on solvent evaporation in order to form a dried or set film, and which film will decompose or break down in the heat of the spraying process. The binder, for example, may be a phenolic varnish or any other known or conventional varnish, preferably containing a resin as the varnish solids. The component which is initially mixed with the binder or varnish should preferably be as finely divided as possible, as for example -325 mesh. The other component which constitutes the core should be approximately or only slightly below the particle size ultimately desired for the spray powder. The coating of the core component with the "paint" may be effected in any known or desired manner, and it is simply necessary to mix the two materials together and allow the binder to dry or set, which will result in a fairly free-flowing powder consisting of the core component coated with a cladding of the other component bound in the binder.

The aggregates may be formed by compacting or

briquetting the various components into the individual granules, or into larger aggregates and then breaking these aggregates into the granules.

The wires may be formed in the known conventional manner for forming wires with various components as, for example, by shrinking a sheath on a core, by forming the core with powder, by twisting the component wires, followed by rolling, drawing, swaging, or the like if desired.

In accordance with one mode of manufacture, one of the components may be formed into a tube or sheath and filled with a powder of the other component or a powder comprising a mixture of the two components, or containing additional components. The tube ends are then sealed and the wire reduced to the desired wire diameter by swaging, rolling or drawing. Preferably the powder or powder mixture is first compressed into cylindrical briquettes before being placed in the sheath or core. The sealing of the tube ends after loading with the powder or powder mixture can be effected, for instance, by insertion of a plug, for example of the metal of the sheath, by welding, twisting, crimping, or the like.

Powders in accordance with the invention should have the general over-all shape and size of conventional, flame-spray powders, and thus for example should have a size between -60 mesh and +3 microns and preferably -140 mesh and +10 microns (U.S. Standard screen mesh size). Most preferably the powder should be as uniform as possible in grain size, with the individual grains not varying by more than 250 microns and preferably 75 microns.

Depending on the particular flame spray process and the desired purpose, the composite powders may be sprayed per se or in combination with other different composite powders, or in combination with other conventional flame spray powders or powder components.

While the powders are preferably sprayed, as such, in a powder-type of flame spray gun, it is also possible to combine the same in the form of a wire or rod, using a plastic or similar binder, which decomposes in the heating zone of the gun, or in certain cases the powders may be compacted and/or sintered together in the form of a rod or wire. The wires must have the conventional sizes and accuracy tolerances for flame spray wires, and thus for example may vary in size between 1/4" and 20 gauge, and are preferably of the following sizes: 5/16" $\pm$ .0005" - .0025", 1/8" $\pm$ .0005" - .0025", 11 gauge $\pm$ .0005" - .0025", and 15 gauge $\pm$ .001", with a smooth, clean finish free from surface marks, blemishes, or defects. The wires are sprayed in the conventional manner, using conventional wire-type flame spray guns.

In combining, in the exothermic reaction, forming the intermetallic compound, the components generate heat in situ in the actual material which is to form at least a part of the coating. This is to be distinguished from flame-spray processes and materials in which heat is generated by a reaction, such as an oxidation reaction, in which a foreign and non-metallic element is introduced and in which undesirable components may be produced. Aside from greatly contributing to the thermal efficiency of the process, the

heat generated *in situ* in the formation of the intermetallic compound produces novel results, in many instances forming a denser, more adhering coating, having characteristics of at least a partially fused coating. In many instances the coating has self-bonding characteristics, so that special surface preparation, other than a good cleaning, is not required. The spraying in all other respects is effected in the conventional, well-known manner, using conventional flame spray equipment, and the conventional surface preparation may be utilized, if desired. The composites in accordance with the invention may be sprayed in conjunction with, or in addition to, other flame spray material conventionally used in the art, or may be sprayed in combination or conjunction with the others.

The use of the composites as, for example, the nickel-aluminum composites, will generally improve the bond of the total sprayed material, and thus of the other component or components to the substrate, sometimes making the mixture self-bonding. The particle bond will be improved and the coating will be denser, so that its porosity may be decreased. In general, as little as 10% by weight of the composites in accordance with the invention will be sufficient to substantially improve the bonding characteristics and decrease the porosity of other flame spray materials, such as conventional flame spray metals, alloys or ceramics. There is, of course, no upper limit on the amount, as the composite may be sprayed per se, but generally at least about 20% by weight of the other component is required if

this component is to have a pronounced effect on the characteristics of the coating.

The following examples are given by way of illustration and not limitation:

EXAMPLE 1

(a) An aluminum powder having a particle size between -140 mesh and +325 mesh (U.S. Standard screen size) is coated with nickel in the known manner by the hydrogen reduction of an ammoniacal solution of nickel and ammonium sulphate, using anthraquinone as the coating catalyst. The reduction is effected at a temperature between about 300 and 350° F. in a mechanically agitated autoclave using solutions containing 40-50 grams per liter of nickel and 10-400 grams per liter of $(NH_4)_2SO_4$ and 20-30 grams per liter of NH_3. About .2 gram per liter of anthraquinone is used as the catalyst and the autoclave is pressurized with hydrogen at a pressure of about 300 lbs. p.s.i.g. After the nickel solution is depleted and the aluminum coated with an initial coating of nickel, the solution is discharged from the autoclave and replenished with a fresh solution which need not contain further amounts of the anthraquinone coating catalyst, as the initially formed nickel coating in itself acts as a catalyst. The cycle is continuously repeated until a composite powder

is formed containing about 16 to 18% by weight aluminum and 84 to 82% by weight of nickel, and a size of -100 to +270 mesh.

The powder thus formed is flame-sprayed on a mild steel plate which has been surface-cleaned with emery cloth. The spraying is effected at about 9 inches from the plate, using a powder-type flame-spray gun as described in U.S. Patent 2,961,335, issued November 22, 1960 and sold by Metco Inc. of Westbury, Long Island, under the trade name of "Thermospray" powder gun. The spraying is effected at a rate of 6 to 9 lbs. of powder per hour, using acetylene gas as the fuel at a pressure of 10 p.s.i. and a flow rate of 17 to 25 cu.ft./hr. and oxygen as the oxidising gas at a pressure of 12 p.s.i. and a flow rate of 29 to 35 cu.ft./hr.

The nickel coating and the aluminum base combine in the heat of the flame with a strong exothermic reaction, forming a mixture of nickel aluminum intermetallic compounds which deposit on the base as a dense, high quality coating which exhibits self-bonding characteristics. A coating layer of .002" $\frac{!}{N}$ .004" thickness is built up in this manner. The coating may be used as a base material for spraying of further layers of different metals or the like, and

47

serves as an excellent intermediate bonding layer.

The coating layer may also be built up to a greater thickness as, for example, .010" - .020", for use as an oxygen barrier undercoat, or to even greater thickness as, for example, .020" - .040" or thicker as a wear-resistant - oxidation-resistant surface.

Due to its self-bonding characteristics, the sprayed coating will adhere to a base without the conventional surface preparation or roughening, and due to the natural characteristics of a sprayed material, will allow further materials to be sprayed thereon with good bonding. The coating formed from the powder has excellent oxidation-resistant characteristics even at high temperatures and in oxidizing atmospheres, and will for example prevent the oxidation of base materials, such as molybdenum or the like. The sprayed coatings may be used as a lining in metal-melting crucibles or molten metal-handling equipment, and will not be wetted or penetrated by many molten metals, including self-fluxing alloys. Coatings formed of the sprayed material also show good potential as high temperature, wear-resistant coatings.

When the example is repeated on a molybdenum rod of 3/18" diameter, with a coating between .010"

.012" thick, the coated rod may be repeatedly heated to approximately 2000° F. in air, in an electric furnace and cooled to room temperature with no visible oxidation occurring.

Similar results may also be obtained if the composite powder contains 10 ~ 45% by weight of aluminum and 55 ~ 90% by weight of nickel.

(b) Example 1(a) is repeated, using, however, cobalt in place of the nickel. Comparable results are obtained.

(c) Example 1(a) is repeated, using titanium hydride (TiH_2) powder in place of the aluminum and in an amount of 25 ~ 85 weight %, and preferably 60 ~ 85 weight % of the total. The coating formed upon spraying is hard and dense, and when sprayed on a smooth, pressed and sintered Al_2O_3 substrate, an excellent bond is formed. The spraying may be effected with an oxygen-hydrogen or oxygen-acetylene flame.

EXAMPLE 2

Example 1 is repeated with the spraying being effected in turn on the following bases and prepared in the following manner:

Low alloy steels and stainless steels, smooth-ground to remove surface contamination; copper and copper base alloys, rough-ground or

light-grit-blasted; aluminum and aluminum base alloys, rough-ground or light-grit-blasted; magnesium, rough-ground or light-grit-blasted; and titanium, rough-ground or light-grit blasted.

In each case when a further material, such as steel, alumina or the like, was sprayed over the coating in the conventional and well-known manner, the same was bonded with a tenacious bond, though if this material had been initially sprayed on the surface as prepared in the manner indicated above, a satisfactory bond would not be obtained.

EXAMPLE 3

The nickel-clad powder of Example 1 is mixed with an Al_2O_3 powder having a particle size between 62 microns and 10 microns, in the ratio of about 40% of the nickel-clad powder with 60% by weight of the ceramic. The powder is sprayed, using the gun described in Example 1, on a mild steel plate which has been surface-cleaned by smooth grinding. Spraying is effected at a distance of about 9" from the plate at a rate of about 4 to 8 lbs. of powder per hr., using acetylene at a pressure of 10 lbs. p.s.i. and a flow rate of 17 ± 25 cu.ft./hr., and oxygen at a pressure of 12 p.s.i. and a flow rate of 29 ± 35 cu.ft./hr.

A self-bonding cermet coating is formed which

showed excellent thermal shock-resistance, hardness, abrasion-resistance, and which strongly inhibited oxidation of the base.

It is possible to vary the percentages of the ceramic in the mixture between 5 and 85% in order to vary the properties of the coating. With an increased amount of the intermetallic compound in the cermet coating formed, the bonding and thermal shock-resistant properties increased, whereas with an increased amount of the ceramic, the hardness and wear-resistant properties of the coating are increased and the thermal conductivity decreased.

EXAMPLE 4

Example 3 is repeated, using the following materials in place of the aluminum oxide:

Zirconia, calcium zirconate, magnesium zirconate, spinel, ceric oxide, hafnium oxide, rare earth oxides, molybdenum disilicide, tungsten silicide, chromium silicide, titanium silicide, tungsten carbide, titanium carbide and chromium carbide.

In each case an excellent coating was formed.

EXAMPLE 5

A nucleus of silicon powder is coated with nickel to form a nickel-clad flame spray powder having a particle size between 100 and 325 mesh

and containing 75 ± 85% nickel based on the silicon-nickel total. The composite powder is sprayed with the flame spray gun described in Example 1 on a steel base prepared by lightly grit-blasting, using the spraying conditions as described in Example 1. During the spraying silicon combines with the nickel in an exothermic reaction, greatly enhancing the thermal efficiency of the spraying and producing an excellent coating.

EXAMPLE 6

Titanium is coated with nickel as described in Example 1 to produce a powder having a particle size between 100 and 325 mesh and containing 10 to 50% nickel based on the titanium-nickel total.

The nickel protects the titanium from oxidation during storage and when spraying.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the nickel and titanium combine exothermically in the flame to form a corrosion-resistant coating comprising a nickel-titanium intermetallic compound.

EXAMPLE 7

Tellurium powder was coated with copper so as to form a composite having a particle size between 100 and 325 mesh and containing 50 to

80% copper based on the tellurium-copper total.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the copper and tellurium combine to form a new material.

During the spraying heat was evolved upon the combination of the copper and tellurium, increasing the thermal economy of the process.

EXAMPLE 8

The nickel-clad flame spray powder of Example 1 is mixed with about 20% by weight of low pressure polyethylene powder and molded at a temperature of about 212° F. into the form of a rod of 1/8" diameter. The rod is sprayed using a conventional wire-type flame spray gun sold by Metco Inc. of Westbury, Long Island, as the Metco-type 4-E gun. The spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu.ft./hr. with oxygen as oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu.ft./hr; with air as a blast gas at a pressure of 40 p.s.i. and a flow rate of 25 cu.ft./min. The end coating produced is similar to the coating produced in Example 1.

EXAMPLE 9

A wire is formed by encasing a core of nickel in a tube of aluminum and drawing to a

size of .125" in diameter plus or minus .002". The wire contains 82 to 84% by weight of nickel based on the aluminum-nickel total.

The wire is sprayed, using a conventional wire type flame spray gun sold by Metco Inc. of Westbury, Long Island, as the Metco-type 4-E gun. Spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu.ft./hr. with oxygen as the oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu.ft./hr. Air is used as a blast gas at a pressure of 55 p.s.i. and a flow rate of 30 cu.ft./min. The end coating produced is similar to the coating produced in Example 1.

Similar results are also obtained using 55 to 90% by weight of nickel in the wire.

EXAMPLE 10

A composite wire is formed by winding individual wires of nickel and aluminum to form a stranded wire with a diameter of .125" plus or minus .002". The wire contains 55 to 90% by weight of nickel based on the total Al-Ni. The wire is sprayed in the manner described in Example 9, with identical conditions and coating resulting.

EXAMPLE 11

A silicon powder having a particle size between 140 and 325 mesh is coated with molybdenum in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The molybdenum coating and the silicon base combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

EXAMPLE 12

A molybdenum powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light

grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type 2MB Plasma Flame Gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using a mixture of argon and hydrogen gas as the plasma gas, with argon at a pressure of 100 p.s.i. and a flow rate of 110 cu.ft./hr., and hydrogen at 50 p.s.i. and a flow rate of 25 cu.ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu.ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57-62 volts.

The molybdenum base and silicon coating combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

EXAMPLE 13

A silicon powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner, and a composite powder is formed containing about 48 to 85% chromium

and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The chromium coating and the silicon base combine in the heat of the flame, forming a chromium-silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

EXAMPLE 14

A chromium powder having a particle size between 140 and 325 mesh is coated with silicon in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type 2MB Plasma Flame

Gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu.ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu.ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57-62 volts.

The chromium base and silicon coating combine in the heat of the flame, forming a chromium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

EXAMPLE 13

A zirconium powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner and a composite powder is formed containing about 45% zirconium and 60% chromium by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material in the manner described in Example 1.

The chromium coating and the zirconium base combine in the heat of the flame, forming a chromium zirconium intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures.

EXAMPLE 16

A titanium powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 65% titanium and 35 to 65% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type 2MB Plasma Flame Gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu.ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu.ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of

400 N 500 amperes at 57 N 62 volts.

The titanium base and silicon coating combine exothermically in the heat of the flame, forming a titanium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

EXAMPLE 17

A dysprosium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 60 to 75% dysprosium and 25 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The aluminum coating and the dysprosium base combine in the heat of the flame with a strong exothermic action, forming a dysprosium aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

EXAMPLE 18

A lanthanum powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 70 to 75% lanthanum and 25 to 30% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the lanthanum base combine exothermically in the heat of the flame with a strong exothermic action, forming a lanthanum aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

EXAMPLE 19

A chromium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed consisting of 60 to 62% chromium and 38 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example-1.

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The aluminum coating and the chromium base combine in the heat of the flame with a strong exothermic action, forming a chromium aluminum intermetallic compound which deposits on the base as a dense, high quality coating of very high melting point and excellent oxidation-resistance.

EXAMPLE 20

Example 19 is repeated except that the composite powder is formed with an aluminum core and chromium coating. Identical results are obtained.

EXAMPLE 21

The nickel-clad aluminum composite powder of Example 1 is mixed with cobalt bonded tungsten carbide particle powder having a particle size range of -140 mesh +10 microns, and preferably -140 +325 mesh in proportions of:

(a) 80 weight percent tungsten carbide to 20 weight percent of the composite.

(b) 20 weight percent of the carbide to 80 weight percent of the composite, and

(c) preferably 50 weight percent each of the tungsten carbide and composite.

The powder mixtures are each flame-sprayed on a mild steel plate which has been surface-cleaned by grinding or very light sand-blast cleaning. The spraying is effected at about 8 - 9 inches from the plate, using a powder-type

flame-spray gun as described in U.S. Patent 2,961,335 issued November 22, 1960, and sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of "Thermo-Spray" powder gun. The spraying is effected at a rate of 6 to 10 lbs. per hour using acetylene gas as the fuel at a pressure of 12 p.s.i. and a flow rate of 20 to 30 cu.ft./hr. and oxygen as the oxidizing gas at a pressure of 14 p.s.i. and a flow rate of 30 to 40 cu.ft./hr.

The nickel-aluminum composite powder in the mixture reacts exothermically in the flame to provide the self-bonding properties of the mixture and, being fully molten on impact with the substrate, becomes the matrix which securely binds the tungsten carbide particles together in the coating.

Used as sprayed, or finished by proper grinding procedure, the resultant coating is of a highly wear-resistant coating material, applicable to virtually any base material and not subject to the limitations of the previously used self-fluxing alloy matrix materials which must be fused at approximately 1900° F.

EXAMPLE 22

Example 21 is repeated except that in place of the grade of tungsten carbide cobalt powder grains used, cobalt-bonded tungsten

carbide grains with lower cobalt content and sharp, angular shape are used.

The powder was sprayed in the manner described in Example 21. The sharp, angular edges of the initial tungsten carbide particles were retained in the coating.

The deposited coating may be suitably finished by grinding for use as a wear-resistant coating or used as deposited where the coated article is to be used as a hone or lap, the sharp edges of the carbide inclusions constituting the abrading or cutting edges.

EXAMPLE 23

Example 22 is repeated except that in place of the tungsten carbide grains described, cobalt-bonded tungsten carbide particles of sharp, angular shape were used which were first coated with nickel in the manner described in Example 1, so as to produce nickel-clad particles having a size between 100 and 325 mesh and containing from 20 $\frac{1}{2}$ 50% nickel based on the tungsten carbide-nickel total.

EXAMPLE 24

The nickel-clad aluminum composite described in Example 1 is mixed with a columbium (niobium) powder of size between -120 mesh and

+10 microns and preferably -140 +325 mesh in the proportions of 60 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and when properly finished, by grinding or other means, is a highly wear-resistant, hard coating.

EXAMPLE 25

The nickel-clad aluminum composite described in Example 1 is mixed with a molybdenum powder of a size between -120 mesh and +10 microns and preferably -140 +325 mesh in the proportions of 65 weight percent molybdenum to 35 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and when properly finished, by grinding or other means, presents a highly wear-resistant, hard surface.

EXAMPLE 26

Example 21 is reposted except in place of the tungsten carbide, other carbides such as titanium carbide, tantalum carbide, columbium

carbide, chromium carbide and mixtures of the various carbides are used.

EXAMPLE 27

The nickel-clad aluminum core composite from Example 21 is mixed with aluminum powder in the mesh size range -100 +325 mesh, and preferably in the -170 +325 mesh size range in the proportions of 80 weight percent nickel aluminum composite to 20 weight percent aluminum.

The mixture was sprayed in the manner described in Example 21. The coating as deposited consists of an intimate mixture of the flame-reacted nickel aluminide and aluminum securely bonded to the base and particle to particle within the coating.

Upon heat-treating in the temperature range 1250° F. to 1500° F. in reducing atmosphere, dry hydrogen for instance, the nickel aluminide and aluminum combine to form a dense, homogenous coating fused to the base material which can be used for "cathodic" protection of iron and steel subject to water and salt-water corrosion.

EXAMPLE 28

The nickel-clad aluminum composite powder of Example 21 is mixed with Monel powder of a size between -100 mesh and +10 microns, and preferably between -140 and +325 mesh in the proportions

35 weight percent composite to 65 weight percent Monel.

The powder mixture was sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and the inclusion of the nickel-aluminum composite, the components of which combine exothermically in the flame to provide the self-bonding ability of the mixture, considerably increase the particle to particle bonds within the coating and decrease the permeability of the coating.

EXAMPLE 29

Example 28 is repeated except that nickel and stainless steel powders are substituted for the Monel.

EXAMPLE 30

Example 28 is repeated except that chromium is substituted for the Monel.

The resultant coating when properly finished, by grinding or other means, shows high resistance to abrasion, wear, and galling by other metals, and is an excellent bearing surface.

EXAMPLE 31

Finely divided aluminum powder (-325 mesh) was blended with a phenolic varnish having approximately

50% solid contents so as to form a mixture having the consistency of a heavy syrup and containing 60% by weight of the metallic aluminum.

100 grams of this varnish aluminum powder mixture was added to 240 grams of nickel powder having a size between -200 and +325 mesh, and the two were thoroughly mixed, with the mixing continued until the varnish dried, leaving a fairly free-flowing powder in which all of the nickel core particles were clad with a dry film, which consisted of aluminum particles bonded to each other and to the core material by the phenolic binder. The powder is then warmed to 250° F. to insure complete drying. There were some minor agglomerates which were screened out and hand-milled to reduce the same to a -100 mesh powder. The end powder consisted of approximately 15 weight % aluminum and 85 weight % nickel due to the loss of some aluminum during the milling. The powder is sprayed in the manner described in Example 1 producing a similar coating having, however, more than twice the tensile strength of the coating produced in Example 1.

EXAMPLE 32

(a) A mixture of 6 weight % aluminum and 94 weight % nickel powder are thoroughly blended and pressed together in the form of cylindrical briquettes which are loaded into an aluminum tube

of .375" outside diameter, after which the tube ends are welded closed. The 3/8" diameter feed stock is then swaged to 1/4" diameter, then to a 3/16" diameter and then to a 1/8" finished wire diameter. The wire is then annealed and coiled. The wire is then sprayed, using the conventional wire type flame spray gun sold by Metco Inc. as the Metco Type 4E Gun. Spraying is effected, using acetylene at a pressure of about 15 lbs. p.s.i. and a flow rate of 37 cu.ft./hr. and oxygen as the oxidizing gas at a pressure of 38 lbs. p.s.i. and flow rate of 75 cu.ft./hr. Air is used as a blast gas at a pressure of 55 lbs. p.s.i. and flow rate of 30 cu.ft./min. The wire is sprayed at a rate of 5 ft. per minute. The spray material is deposited on a surface of ground and machine-finished, cold rolled steel with a tensile bond strength of 3820 lbs. p.s.i. The sprayed coating is hard and dense; it is wear- and oxidation-resistant and it also could serve as a base for further spraying.

(b) Example 32(a) is repeated except that chromium is used in place of the nickel powder in amounts of from 24 to 95 weight %, based on the total of the aluminum and chromium. Spraying results in a high quality coating which has self-bonding properties and is resistant to oxidation at high temperatures.

(c) Example 32(a) is repeated, using columbium powder in place of the nickel powder in amounts of from 40 -/+ 90 and preferably 50 -/+ 55 weight %, based on the total of the columbium and aluminum. The sprayed coating formed is a high quality coating which is resistant to oxidation at high temperatures and may be used to protect tantalum and molybdenum bases from oxidation.

(d) Example 32(a) is repeated, using tantalum powder in place of the nickel powder in amounts of 40 -/+ 90 weight % and preferably 65 -/+ 75 weight % of tantalum, based on the total of tantalum and aluminum. The sprayed coating is a dense, high quality coating which is self-bonding and is resistant to oxidation at high temperatures.

(e) Example 32(a) is repeated, using boron powder in place of the nickel powder in amounts of 40 -/+ 90 weight %, based on the total of boron and aluminum. The resulting sprayed coating is self-bonding and is resistant to oxidation at high temperatures.

(f) Example 32(c) is repeated except that the powder additionally contains 0.5 to 5 weight % of boron, and/or 0.5 to 5 weight % of silicon, based on the total of the components. The coating formed is similar to that obtained in Example 32(c) except that on heating to high temperature in air,

a very thin, dense, adherent, protective oxide film forms on the surface of the intermetallic compound formed, which is resistant to spalling due to thermal shock, and which is believed self-healing.

(g) Example 32(a) is repeated except that tungsten carbide containing 12% binder and having a particle size below -140 mesh is added in amount of 5 ! 70 weight % based on the total of the components. The resulting coating is a dense, extremely wear-resistant coating, which has self-bonding properties. This example may be further repeated, using in place of the tungsten carbide specified, crystalline tungsten carbide, aluminum oxide, diamonds or any other abrasive material.

(h) Example 32(a) is repeated. However, 1 ! 10% by weight and preferably 1 ! 5% by weight of titanium hydride of a size below -100 mesh and preferably below -325 mesh, based on the total of the components, is added to the core material. The results are the same as indicated in Example 32(a) except that the coating formed is of improved physical strength, containing considerably less oxide inclusions. In place of the titanium hydride other metal hydrides may be used.

(i) Example 32(a) is repeated except that the nickel powder is replaced with a nichrome powder consisting of a chrome alloy containing 80% nickel and 20% chromium. When sprayed the wire gives a

dense, self-bonding coating which is extremely oxidation-resistant.

(j) Example 32(a) is repeated except that the nickel powder is replaced with a powder mixture consisting of 80% by weight nickel and 20% by weight chrome. When sprayed the wire gives a dense, self-bonding coating which is highly oxidation-resistant.

EXAMPLE 33

Table I below gives examples of further component pairs which may be used to form the powders and/or wires in accordance with the invention.

Each of the component pairs as listed in Table I below may be formed into a composite powder or wire as described above, and when flame-sprayed will exothermically react, forming an intermetallic compound and high grade coating. Thus, the component pairs may be formed into clad powders as described in Example 31 and sprayed as described therein, or formed into a composite wire as described in Example 32 and sprayed as described therein.

Table I (cont'd)

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Ag Ce	As In	Bi Mg	In Te	Pb Pu			
Al As	As Mg	Bi Na	In Ru	Pb Se			
Al Au	As Zn	Bi Se	K Sb	Pb Tl			
Al B	B Y	Bi Te	K Se	Pd U			
Al Ba	B Co	Bi Th	K Sn	Pr Sn			
Al Ca	B Cr	Ca Pb	K Te	Pr Tl			
Al Ce	B Hf	Ca Sn	La Pb	Sb Zr			
Al Co	B Nb	Ca Tl	La Sb	Se Sn			
Al Cr	B Ta	Cd Li	La Sn	Se Th			
Al La	B Th	Cd Na	La Te	Se Tl			
Al Li	B Ti	Ce In	La Zn	Cu Te			
Al Mo	B V	Ce Mg	Li Pb	Si Ti			
Al Nb	B W	Ce Pb	Li Sb	Si U			
Al Ni	B Zr	Ce Si	Li Sn	Si V			
Al Pr	Ba Bi	Ce Sn	Li Tl	Si Zr			
Al Ti	Ba Pb	Ce Tl	Li Zn	Sn Te			
Al Zr	Ba Sb	Ce Zn	Mg Sb	Sn U			
Al Sb	Be Co	Ga Na	Mg Sn	Sn Zr			
Al Se	Be Cr	Ga Pr	Na Pb	Te Zn			
Al Ta	Be Ni	Ga Sb	Na Sb	Mg Be			
Al Te	Be Np	Ga Te	Na Se	Nb Be			
Al U	Be Pu	Ga U	Na Sn	Ta Be			
Al V	Be U	Ge Mg	Na Te	V Be			
Al W	Be Zr	Ge Nb	Na Tl	Ti Be			
As Cd	Bi Ca	Ge Zr	Nb Si	Cr Si			
As Ba	Bi Ca	H V	Ni Th	Cr Ti			
	Bi K	Li In	Pb Pr	Cr Zr			
	Bi Li						

Table I (continued) E 745

Mg	Te
Ni	Te
Si	Th
Si	W
Co	Si
Mo	Si
Ni	Si
Si	Ta

While the invention has been described in detail with reference to certain specific embodiments, various changes and modifications which fall within the spirit of the invention and scope of the appended claims will become apparent to the skilled artisan. The invention therefore is only intended to be limited by the appended claims or their equivalents, wherein we have endeavored to claim all inherent novelty.

We claim:

We claim: (repeated)

1. In the flame spray process in which a heat-fusible material is heated in a heating zone to at least a heat-softened condition and propelled in such condition out of said zone in finely divided form onto a substrate, the improvement which comprises passing the heat-fusible material into said zone in the form of a composite comprising at least two distinct unalloyed components in proportion and form sufficient to ~~which~~ exothermically react with each other at the temperature developed in the heating zone, forming an intermetallic compound.

2. Improvement according to claim 1 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.

3. Improvement according to claim 1 in which said components are components which exothermically react with each other, with the release of at least 7,500 gram calories per gram atom.

4. Improvement according to claim 1 in which one of said components is aluminum and the other nickel.

5. Improvement according to claim 4, in which said aluminum is present in amount of about 10 to 43% by weight, based on the total of nickel and aluminum.

6. Improvement according to claim 1 in which said components are component pairs selected from the group listed in Table 1 above.

7. Improvement according to claim 1 in which said composite contains at least one additional flame spray material.

8. Improvement according to claim 1 in which said composite is sprayed in conjunction with at least one further flame spray material.

9. In the flame spray process in which heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form onto a substrate, the improvement which comprises passing the heat-fusible material into said zone in the form of individual clad powder particles comprising a nucleus and a coating layer which will exothermically react with the nucleus at the temperature developed in the heating zone, forming an intermetallic compound.

10. Improvement according to claim 9 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.

11. Improvement according to claim 9 in which said components are components which exothermically react with each other, with the release of at least 7,500 gram calories per gram atom.

12. Improvement according to claim 9 in which said nucleus is aluminum and said coating layer nickel.

13. Improvement according to claim 12 in which said aluminum is present in amount of about 10 $\frac{L}{N}$ 45%, based on the total of nickel and aluminum.

14. Improvement according to claim 9 in which the nucleus and coating layers are selected from the members of the group consisting of the pairs listed in Table I.

15. Improvement according to claim 9 in which said coating layer consists of fine particles bound to said nucleus by a binder.

16. Improvement according to claim 9 in which said clad powder particles are in admixture with another flame spray powder.

17. In the flame spray process in which heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form onto a substrate, the improvement which comprises passing the heat-fusible material into said zone in the form of a composite, non-cavitating wire comprising at least two components which exothermically react with each other at the temperatures developed in the heating zone, forming an intermetallic compound.

18. Improvement according to claim 17 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.

19. Improvement according to claim 17 in which said components are components which exothermically react with each other, with the release of at least 7,500 gram calories per gram atom.

20. Improvement according to claim 17 in which one of said components is aluminum and the other nickel.

21. Improvement according to claim 20 in which said aluminum is present in amount of about $10\frac{1}{N}$ - 45% by weight, based on the total of nickel and aluminum.

22. Improvement according to claim 17 in which said components are component pairs selected from the group listed in Table I above.

23. Improvement according to claim 17 in which said wire is in the form of a sheath of one component containing a powder of the other component, said sheath being of a component having a lower melting point than the other component.

24. Improvement according to claim 23 in which said sheath is an aluminum sheath and in which said core is a compacted mixture of aluminum and nickel powder.

25. Improvement according to claim 17 in which said wire is a multi-strand wire with individual strands of said components.

26. A flame spray material suitable for use in the process of claim 1, comprising a composite containing at least two components which exothermically react with each other when melted, forming an intermetallic compound.

27. A flame spray material suitable for use in the process of claim 1, comprising a composite containing at least two components which exothermically react with each other when melted, forming an intermetallic compound with the release of at least 3,000 gram calories per gram atom.

28. A flame spray material suitable for use in the process of claim 1, comprising a composite containing at least two components which exothermically react with each other when melted, forming an intermetallic compound with the release of at least 7,500 gram calories per gram atom.

29. A flame spray material suitable for use in the process of claim 1, comprising a composite containing aluminum and nickel.

30. Composite according to claim 29 in which said aluminum is present in amount of about 10 - 45%, based on the total of nickel and aluminum.

31. Composite according to claim 26 in which said components are component pairs selected from the group listed in Table I above.

32. A flame spray powder in the form of individual clad particles comprising a nucleus and at least one coating layer of a material differing from said nucleus and exothermically reactive therewith when melted together, forming an intermetallic compound.

33. A flame spray powder in the form of individual clad particles comprising a nucleus and at least one coating layer of a material differing from said nucleus and exothermically reactive therewith when melted together, forming an intermetallic compound, with the release of at least 3,000 gram calories per gram atom.

34. A flame spray powder in the form of individual clad particles comprising a nucleus and at least one coating layer of a material differing from said nucleus and exothermically reactive therewith when melted together, forming an intermetallic compound, with the release of at least 7,500 gram calories per gram atom.

35. A flame spray powder according to claim 32 in which said components are component pairs selected from the group listed in Table I above.

36. A flame spray powder according to claim 32 in which said coating layer is in the form of a finely divided powder bound to the nucleus by a binder.

37. A flame spray powder in the form of individual clad particles comprising a nucleus of aluminum and a coating layer of nickel.

38. Powder according to claim 37 in which said aluminum is present in amounts of about 10 - 45%, based on the total of nickel and aluminum.

39. A flame spray powder in the form of individual clad particles comprising a nucleus of nickel and a coating layer of finely divided aluminum particles bound to the nucleus with a binder.

40. A non-cavitating flame spray wire suitable for use in the process of claim 1, comprising two separate components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound.

41. A non-cavitating flame spray wire suitable for use in the process of claim 1, comprising two separate components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound, with the release of at least 7,500 gram calories per gram atom.

42. A non-cavitating flame spray wire suitable for use in the process of claim 1, comprising two separate components differing from each other and capable of exothermically reacting with each other when melted together, one of said components being aluminum and the other nickel.

43. A flame spray wire suitable for use in the process of claim 1, comprising two separate components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound, with the release of 7,500 gram calories per gram atom, said components being component pairs selected from the group listed in Table I above.

44. A flame spray wire suitable for use in the process of claim 1, comprising a sheath of a first component and a powder core of at least one second component, said first and second components being capable of exothermically reacting with each other when melted together, with the release of at least 7,500 gram calories per gram atom.

45. A flame spray wire according to claim 44 in which said sheath is aluminum and said core a mixture of aluminum and nickel powder.

46. A flame spray wire suitable for use in the process of claim 1, comprising individual strands of two separate components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound, with the release of at least 7,500 gram calories per gram atom.

47. 26 Improvement according to claim 1 in which the heat-fusible material additionally contains a metal hydride.

48. 27 Process according to claim 47 in which one of said components is at least partially in the form of a hydride.

~~49. Flame spray material according to claim 26~~ additionally containing a metal hydride.

50. Flame spray material according to claim 26 in which one of the said components is at least partially in the form of a hydride.

51. Flame spray material according to claim 26 additionally containing a member selected from the group consisting of boron, silicon and mixtures thereof.

52. A flame spray material suitable for use in the process of claim 1, comprising a composite containing at least two components which exothermically react with each other when melted, said components being component pairs selected from the group consisting of Al Co, Al Cr, Al Mo, Al W, Al Ta, Al Nb, Al Ti, Al Ni, Si Nb, Si Cr, Si W, Si Co, Si Mo, Si Ni, and Si Ta.

53. A flame spray material according to claim 32 in the form of a powder.

54. A flame spray material according to claim 32 in which one of the components is in the form of a coating on the other component.

55. A flame spray material according to claim 32 in the form of a wire.

DECLARATION, POWER OF ATTORNEY and PETITION

We, FERDINAND J. DITTRICH and ARTHUR P. SHEPARD, declare that we are respectively citizens of United States, residing respectively at 2457 New Place, Bellmore, Long Island, New York, and 29-01 - 159th Street, Flushing, Long Island, New York; that we have read the foregoing specification and claims and verily believe that we are the original, first and joint inventors of the improvement in FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES described and claimed therein; that this application in part discloses and claims subject matter disclosed in our earlier filed pending applications, Serial No. 72,543 filed November 22, 1960; Serial No. 134,544 filed August 16, 1961; Serial No. 237,786 filed October 26, 1962; and Serial No. 343,705 filed February 10, 1964; that as to the subject matter of this application which is common to said earlier applications we do not know and do not believe that the same was ever known or used before our invention thereof or patented or described in any printed publication in any country before our invention thereof or more than one year prior to said earlier applications, or in public use or on sale in the United States for more than one year prior to said earlier applications; that said common subject matter has not been patented before the dates of said earlier applications in any country foreign to the United States on any application filed by us or our legal representatives or assigns more than twelve months prior to said applications; that as to the subject matter of this application which is not common to said earlier applications, we do not know and do not

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believe that the same was ever known or used before our invention thereof or patented or described in any printed publication in any country before our invention thereof or more than one year prior to this application, or in public use or on sale in the United States for more than one year prior to this application, and that said subject matter has not been patented in any country foreign to the United States on an application filed by us or our legal representatives or assigns more than twelve months prior to this application; and that no application for patent on said invention has been filed by us or our representatives or assigns in any country foreign to the United States, except as follows: Argentina, filed September 14, 1961; Belgium, filed November 21, 1961; France, filed November 17, 1961; Spain, filed September 29, 1961; Australia, filed September 19, 1961; Canada, filed November 8, 1961; Germany, filed October 24, 1961; Great Britain, filed September 14, 1961; Holland, filed October 13, 1961; India, filed August 22, 1961; Italy, filed September 27, 1961; Japan, filed November 22, 1961; Mexico, filed October 20, 1961; Sweden, filed October 27, 1961; Switzerland, filed October 31, 1961; India filed May 21, 1963.

And we hereby appoint BURGESS, DINKLAGE & SPRUNG, Registration No. 15,379, a firm composed of Ralph D. Dinklage and Arnold Sprung, of 605 Third Avenue, New York, New York 10016, our attorneys with full power of substitution and revocation to prosecute this application and to transact all business in the Patent Office connected therewith.

55

WHEREFORE we pray that Letters Patent be granted to us for the invention or discovery described and claimed in the foregoing specification and claims, and we hereby subscribe our names to the foregoing specification and claims, declaration, power of attorney and this petition.

The undersigned petitioners declare further that all statements made herein of their knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Inventor's full name FERDINAND J. DITRICH

Date 22 March 1965 Ferdinand J. Ditrich
(Signature)

Post Office Address: 2457 New Place, Bellmore, Long Island, New York.

Inventor's full name ARTHUR P. SHEPARD

Date 22 Mar. '65 Arthur P. Shepard
(Signature)

Post Office Address: 29-01 - 159th Street, Flushing, Long Island, New York.

PRINT OF DRAWING AS
ORIGINALLY FILED

E 759

592238

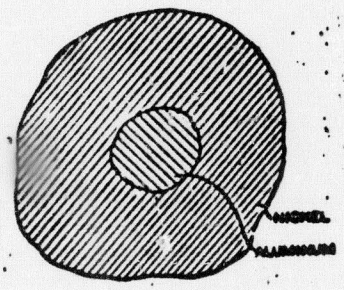

Fig. 1

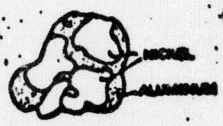

Fig. 2

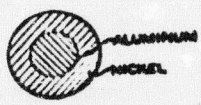

Fig. 3

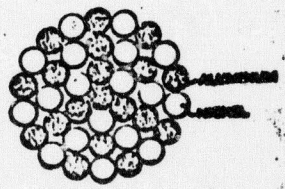

Fig. 4

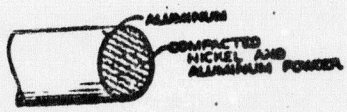

Fig. 5

INVENTORS
FERDINAND J. SYTTKUS.
ARTHUR R. SHEPARD
BY Burgess, Dinklage & Sprung
ATTORNEYS

PHOTOPRINTS AS DRAWINGS
FOR FILING DATE ONLY

57

105.1
3,436,248
PRINT OF DRAWING AS ORIGINALLY FILED
E 760
GR 160 M1

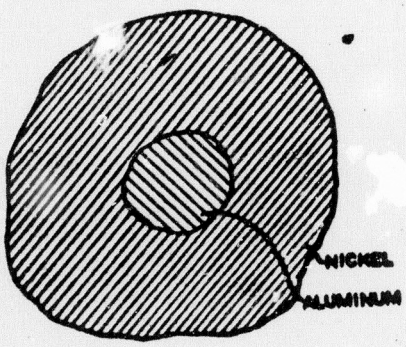

Fig. 1

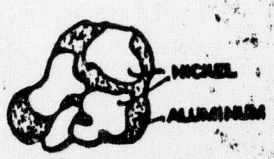

Fig. 2

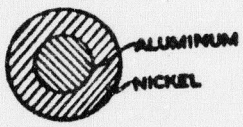

Fig. 3

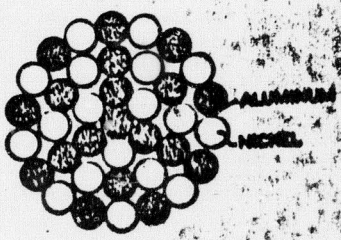

Fig. 4

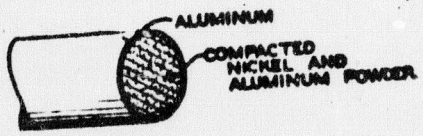

Fig. 5

INVENTORS,
FERDINAND J. DITTRICH
ARTHUR R. SHEPARD
BY Bacigalupo, Dinkelacker & Spaeth
ATTORNEYS

UNITED STATES PATENT

JUN 3 1966 U.S. PATENT OFFICE

E 761

June 2, 1966

Honorable Commissioner of Patents
Washington, D. C. 20231

Dear Sir:

Re: Our File Matco 305.5

On May 25, 1966 a request was made, under the provisions of Rule 147, for the Office to prepare a certified copy of the following application:

Serial No.: 442,727
Filed: March 25, 1965
By: Ferdinand J. Dittrich et al.
For: Flame Spraying Exothermically Reacting Intermetallic Compound Forming Composites

Such certified copy is intended to serve as the formal papers of a new divisional application.

We now respectfully request that the enclosed Brisol board drawing be entered in the divisional application in order to complete all requirements.

Very truly yours,

Burgess, Dinklage & Sprung

BURGESS, DINKLAGE & SPRUNG

605 Third Avenue
New York, New York 10016

Parmelee, Dinklage and Sprung
605 Third Avenue
New York, N. Y. 10016

Gentlemen:

On May 26, 1966 this Office received [illegible]
for a certified copy of the parent application
finally filed and a proposed amendment in the application
in the names of Ferdinand J. Dittrich and Arthur J. Shepard
for Flame Spraying Exothermically Reacting Intermetallic
Compound Forming Compositions, as a division of application
Serial Number 448,727, under the provisions of Rule 47.
Your Docket No. Metco 305.

The certified copy of the parent application and also will be prepared in compliance with your request and the divisional application given a filing date of May 26, 1966.

A formal sheet of drawing was also received June 1, 1966.

Sincerely yours,

R. J. ROSENBAUM
HEAD, APPLICATION BRANCH

THE COMMISSIONER OF PATENTS
WASHINGTON, D.C. 20231

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

E 763 Dec. 5, 1966

Burgess, Dinklage and Sprung
605 Third Avenue,
New York, N. Y. 10016

In re application of:

Dittrich, Ferdinand J. and
Shepard, Arthur P.
FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC
COMPOUND FORMING COMPOSITES
S.N. 592 238
Filed: May 26, 1966

The formal drawings have been compared with the photoprints filed with the application.

The drawings have been approved and forwarded with the application for examination.

☒ The comparison charge of $10.00 has been applied against your deposit account.

☐ The initial $10.00 payment has been accepted as the comparison charge.

Sincerely yours,

R. J. Rosenbaum

Head, Application Branch

Your application has been forwarded to Group 111.

POL-286 (10-64)

USCOMM-DC 7882-P64

MAIL ROOM MAR 31 1967 U.S. PAT.

GROUP 110

IN THE UNITED STATES PATENT OFFICE E 764

Applicants : Ferdinand J. Dittrich and Arthur P. Shepard

Serial No. : 592 238

Filed : May 26, 1966 Group 111

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

March 27, 1967

Hon. Commissioner of Patents
Washington, D. C. 20231

Sir:

Kindly enter the following amendment in the above application:

Cancel claims 26 through 46 and 49 through 56.

REMARKS

The above amendment cancels the claims prosecuted in the parent application, Serial No. 442 727.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By: _____
Attorneys for Applicants

ADDRESS ONLY
THE COMMISSIONER OF PATENTS
WASHINGTON, D.C. 20231

E 765

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

Paper No. 3

In Reply Please Refer To The Following And Furnish Your Zip Code:	Group
	161
Applicant: Ferdinand J. Dittrich et al.	
Ser. No. 592,238	Mailed
Filed May 26, 1966	
For FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES	

Burgess, Dinklage and Sprung
605 Third Avenue
New York, N.Y. 10016

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

This application has been examined.

Note attachment: List of References.

1) An abstract is required, see new Rule 72(b).

2) The current status of the applications set forth on paragraph 1 on page 1 of the specification is required to be inserted.

3) Claims 1 to 25, 47 and 48 are rejected as vague and indefinite in failing to properly define the invention as required under 35 USC 112. Claims 1 to 20, 47 and 48 are unduly broad in failing to recite that a coating is applied onto a substrate. Claims 7 and 8 are considered duplicates.

4) Claims 1 to 4, 6 to 8, 17 to 22 are rejected as unpatentable over Shepard per se or further in view of Boggs under 35 USC 103. Shepard teaches the process of applying in a metal spray process nickel and aluminum (See claim 1) with an additional component such as boron. Since Shepard teaches heating of the material during the spray operation, the process is seen to be a flame spraying operation. In any case Boggs is applied to teach that it is

old to flame spray plural metal components. To apply the coating of Shepard by flame spraying is seen obvious.

5) Claims 1 to 8, 47 and 48 are rejected as unpatentable over White et al. in view of Hertz under 35 USC 103. White et al. is applied to teach that it is old to apply flame spray coatings of exothermically reacting materials. The Hertz reference teaches that nickel will react with aluminum exothermically when heated to form an intermetallic compound. Also Hertz teaches that other components may be employed such as zirconuim hydride. It would be within the ordinary skill of one in the art to employ the composition of Hertz in the teachings of White et al. of flame spraying an exothermically reacting composition to form a coating upon a substrate.

6) Claims 9 to 16 are rejected as unpatentable over the reference (s) and reasons applied in either paragraph 4 and 5 further in view of Shwayder under 35 USC 103. The Shwayder reference is applied to teach that flame spraying of coated particles is old in the art. To apply the technique of Shwayder of flame spraying coated component powders in the process of the teaching of the references applied in paragraphs 4 and 5 is seen obvious.

7) Claims 17 to 22 are rejected as unpatentable over the references and reasons applied in paragraph 5 supra, further in view of Shepard under 35 USC 103.

Shepard is applied to teach that metal materials may be sprayed in either wire of powder form utilizing a binder. To apply the equivalent teachings of Shepards in the process of Hertz and White et al. is seen well within the ordinary skill of one in the art. It is pointed out thatboth powder and wire feed materials are both commonly used in flame spraying.

8) Claims 23 to 25 are rejected over the reference(s) and reasons applied in either paragraphs 4 and 7 under 35 USC 103. Applicant chooses to claim assheath containing the powder. This expedient in absence of unexpected results, is seen to be an obvious variation of the basic process. To spray both powders and wires are known. To combine a powder with a wire in a single process for its expected results is seen within the ordinary skill of one in the art. With regard to claim 25 note Bleakley wherein use of multi-strand wires are employed in flame spraying.

9) Claims 47 and 48 are rejected as unpatentable over the references and reasons applied in paragraph 47 further in view of Herz under 35 USC 103. Herz teaches that a metal hydride may be employed in the exothermically reacting mixture. It is well recognized that the hydride is heat decomposible to form the metal. To employ a metal hydride in the references previously employed is seen to be an obvious variation of the basic flame spray process.

10) The Bleakley, Mackiw et al. Broadstreet, Bayer and Joseph references cited of interest, all teach application of various coating materials by spraying including flame spraying while Grala et al. teaches use of nickel aluminum components.

Summary:

Claims rejected: 1 to 25, 47 and 48.

Claims allowed: None

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS ACTION IS SET TO EXPIRE THREE MONTHS FROM THE DATE OF THIS LETTER.

AGolian:hrc

(703) 521-5600
Ext.3697

ALFRED L. LEAVITT
EXAMINER

L 109

TO SEPARATE, HOLD [redacted] AND BOTTOM EDGES, SNAP-APART AND D[redacted]RD CARBON

Form PO-892 (6-67) U.S. DEPARTMENT OF COMMERCE PATENT OFFICE

NOTICE OF REFERENCES CITED

[redacted]

Check here if this is a supplemental citation ☐
(Do not prepare an additional folder)

APPLICATION SERIAL NO. 592,235 | Art Unit 261

[redacted] Applicant(s)

DITTRICH ET AL

U. S. PATENTS

	PATENT NO.	DATE	PATENTEE	CLASS	SUB-CLASS	FILING DATE IF APPROPRIATE
1	2,231,947	2/41	DEARLEY	117	106; 51	
2	2,853,403	9/58	MACKIW ET AL.	117	[illegible]	
3	2,884,688	5/59	HERZ	75	[illegible]	
4	2,904,449	9/59	BRADSTREET	117	46 FS	
5	2,910,356	10/59	GRALA ET AL.	75	[illegible]	
6	2,936,229	5/60	SHEPARD.	75	[illegible]	
7	2,976,166	3/61	WHITE ET AL.	117	[illegible]	
8	2,988,807	6/61	BOGGS.	117	[illegible]	
9	3,049,435	8/62	SCHNAYDER	117	122	
10	3,050,409	8/62	BAYER.	117	122	
11	3,102,044	8/63	JOSEPH	117	122	

FOREIGN REFERENCES*

	PATENT NO.	DATE	COUNTRY	NAME	CLASS	SUB-CLASS	PERTINENT SHTS. DWG.	PERTINENT PG. SPEC.
1								
2								
3								
4								
5								
6								

OTHER REFERENCES (Include author, title, date, pertinent pages, etc.) *

Exam[illegible] | Date [illegible]

E 770

IN THE UNITED STATES PATENT OFFICE

RECEIVED
JAN 22 1968
GROUP 160
Group 161

Applicants : Ferdinand J. Dittrich et al.

Serial No. : 592,238

Filed : May 26, 1966

For : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Jan. 15, 1968

Hon. Commissioner of Patents
Washington, D.C. 20231

Sir:

The following is in response to the Office Action dated December 11, 1967. Kindly enter the following amendment:

Specification, page 1, line 2, after "November 22, 1960" insert --, now abandoned--

line 3, after "August 16, 1961" insert -- issued to U.S. Patent 3,254,970--

line 4, after "October 26, 1962" insert -- , now abandoned--

line 5, after "February 10, 1964" insert -- , now abandoned--

Claim 1, line 4, after "form" insert --onto a substrate--

Claim 9, line 4, after "form" insert --onto a substrate--

Claim 17, line 4, after "form" insert --onto a substrate--

REMARKS

The status of the applications set forth in paragraph 1, page 1 of the specification, has been inserted as requested.

The claims have been amended in order to overcome the Examiner's rejection thereto as set forth in paragraph 3 of the Action. With respect, however, to claims 7 and 8, it is submitted that the same are not duplicates. Claim 7 requires that the composite contain at least one additional flame-spray material, i.e. that this material be directly incorporated in the composite, while claim 8 calls for the spraying in conjunction with a further flame spray material. Thus, in accordance with claim 8, the composite and additional flame-spray material may be admixed as separate particles in a powder mixture, or even sprayed at the same time from separate guns.

In accordance with the applicant's invention, the flame spraying is effected utilizing as the flame spray material, a composite containing at least two components which will exothermically react with each other at the temperature developed in the heating zone to form an intermetallic compound. The term "composite" as used in the specification (see page 5, 2nd full paragraph) defines a structurally integral unit in which the components are integrally bound together in contact with each other as a unit, as for example in the form of the coated powder particles, or aggregate grains, or the wire. The mere mixture of the components is not included in this designation. In accordance with the invention, when spraying utilizing the composite containing the components

which will exothermically react to form the intermetallic compound, new and unexpected results are obtained. The components of the composite react during the spraying operation liberating heat and aiding in the process, such as in the bonding to the substrate.

As is well known in the flame spray art, the bonding of the spray particles to the substrate has presented a major difficulty and problem. The bonding gnerally occurs in a mechanical fashion, and in order to achieve a satisfactory bonding, the surface had to be extensively prepared by exhaustive surface roughening, mechanical threading or the like, so that the sprayed particles would actually interlock with the cavities formed by the roughening.

It was later discovered that molybdenum would adhere to a substrate without this extensive mechanical roughening and molybdenum was thus unique in what was considered as a self-bonding effect for a flame spray material. With the spraying of the composites in accordance with the invention, the bonding is greatly enhanced and composites, such as the nickel aluminum composites, are self-bonding even to a greater extent than molybdenum and have already achieved widespread commercial success as a bonding coating material.

None of the references cited by the Examiner disclose the flame spraying of a composite containing components which will exothermically react to form an intermetallic compound, and none of the references, either singly or in

combination, teach a process capable of achieving the novel results obtained by the claimed process.

The Shepard patent of record simply relates to the spraying of an alloy which may contain nickel and a minor quantity of aluminum. The material is used in the sprayweld process, in which process the material is initially deposited by flame-spraying and then fused in place. The aluminum produces a killing effect to prevent pore formation during the subsequent fusing operation. The aluminum is already alloyed with the other components and cannot and does not exothermically react therewith during the spraying operation. Thus the aluminum and the nickel are not separate components in the composite but are alloyed together and thus constitute a completely different material. The Examiner can well appreciate that if the components are already combined, they cannot exothermically react in a combining reaction.

The Boggs reference of record relates to the spraying of a mixture of aluminum and copper. As pointed out, the spraying of a powder mixture of the components will not produce the applicants' effect and has no relation to the applicants' invention. In accordance with the applicants' invention, the individually sprayed particles must react en route to the substrate and, as can well be appreciated, individual particles of the separate components are not in individual contact to allow this.

The White et al. patent relates to an exothermic

reaction of the oxidation type in which oxygen must be incorporated for the temperature generation. Except for the special case in forming oxide coatings, the incorporation of an oxide in a flame spray coating is undesirable, forming an oxidized coating. Furthermore, the addition of the oxygen and the oxidation will generally distract rather than aid in the bonding. In accordance with the novel features of the applicants' invention, the exothermic reaction occurs without the incorporation of any hetro atoms, such as oxygen, and the end coating in spite of the heat generation is purely metallic.

The Hertz reference has been cited to show that nickel and aluminum will combine to form an intermetallic compound in an exothermic reaction. This was of course admittedly old and textbook knowledge. There is nothing, however, in the Hertz patent per se, or in combination with the other references, which would teach the use of a composite containing such exothermically reacting intermetallic components in a flame spray process, or that any beneficial results could be obtained therefrom. Furthermore, there is no teaching in the Hertz reference of forming a composite of the components in a form which could be flame-sprayed.

The Schwayder reference simply relates to the coating of tungsten carbide particles with a nickel matrix in order to bind the articles to the surface. There is nothing in this reference which is even remotely suggestive of the flame spraying of the composite containing the exothermically

reacting intermetallic compound forming the components, and the coating of tungsten carbide with a conventional matrix therefor, i.e. nickel, could not suggest this in combination with the other references.

With respect to the rejection as set forth in paragraph 7 of the action, Shepard has been cited to show that it is known that metal materials may be sprayed as a wire formed of particles using a binder. It is, of course, well known that flame spray material may be utilized in powder form or in wire form, and the wire may be formed of powder particles bound together. This, however, did not indicate the spraying of material in any of these forms containing the exothermically reacting intermetallic forming components structurally bound together as a composite, which specific form produces the new and unexpected results in accordance with the invention.

With respect to the rejection as set forth in paragraph 8, it is pointed out that this form of the wire has proven particularly advantageous and produces superior results. It is in this form that the applicants' assignee has commercially utilized the invention insofar as the wire type flame spray material is concerned.

As the references do not, singly or collectively, teach the spraying of the composites as claimed, the same obviously would clearly not teach the spraying of such composites containing a metal hydride additionally or as one of the components, as set forth in claims 47 and 48.

While the Bleakley, Mackiw et al., Bradstreet, Bayer, Joseph and Grala et al. references have merely been cited of interest, it is pointed out that none of these references teaches or indicates the spraying of the specific claimed composite combination or that beneficial results could be obtained therefrom

In view of the above, reconsideration and allowance of the claims as amended, are hereby solicited.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

BY _____

Attorneys for Applicants

THE COMMISSIONER OF PATENTS
WASHINGTON, D.C. 20231

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

Paper No. 7

E 777

Burgess, in lage and Sprung
605 Third Avenue
New York, N. Y. 10016

In Reply Please Refer To The Following And Furnish Your Zip Code:

Examiner's Name	Group Art Unit
A. Golian	161

Applicant: Ferdinand J. Dittrich et al.

Ser. No.	Mailed
592,238	MAILED
Filed: May 26, 1966	FEB 13 1968

For: FLAME SPRAYING ETHOTHERMICALLY RE-ACTING... COMPOSITES

GROUP 160

SHORTENED TIME FOR REPLY

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

A SHORTENED STATUTORY PERIOD FOR RESPONSE TO THIS ACTION IS SET TO EXPIRE 3 MONTHS, ~~DAYS~~ FROM THE DATE OF THIS LETTER.

Responsive to the amendment filed January 16, 1968.

1.) The rejection of claims 1 to 5, 7, under 35 U.S.C. 103 has been set forth in paragraphs 4 to 8 in the Office action of December 11, 1967, and this rejection is incoporated by reference herin. The rejection set forth in these paragraphs has been reconsidered in view of applicant's arguments. However the rejection is seen sound, adhered to and made FINAL.

2.) Applicant urges on page 27 the amendment of January 16, 1968 that the definition of "composite" as set forth on page 5, 2nd full paragraph defines a structural integral unit in contrast to a mere mixture which may be physically separated. No issue is taken with applicant's position concerning this definition. However, it is pointed out that it is conventional in the

2/6

art to flame spray an admixture of separable particles or spray such mixture in a form that cannot be separated easily as in the shape of a wire. Furthermore applicant has not shown any difference in results between a separate admixture and a non-separable composite. Applicant's attention is directed, for example, to Shepard on the paragraph bridging columns 5 and 6 wherein a separable powder mixture is flame sprayed and Example 6 of this patent wherein a wire composite is employed which materials cannot be separated without destruction of the wire.

3.) Applicant sets forth the position that none of the references teach flame spraying of materials that will exothermically react to form an intemetallic compound. It is reiterated that the rejection set forth previously is seen sound. For example Shepard on the first Table on column 2 set forth a nickel alloy containing as high as 98% nickel. Applicant concedes that Shepard teaches flame spraying. The addition of aluminum in powder form to the nickel alloy is seen to provide an exothermically reacting mixture. Direct issue is taken with applicant's position that the aluminum must be combined with the nickel prior to the flame spray process. Attention is specifically directed to column 3, lines 62

to 65 and Example 5 of Shepard.

4.) Also as taught by While et al. it is old in the art to employ exothermically reacting materials in flame spraying to form a coating and to employ specific metals known as exothermically reacting in the process of White et al. is seen well within the ordinary skill of one in the art. Obviously if a metal RATHER than a metal oxide is desired, oxygen will be excluded to prevent oxidation of the metal in White et al.

5.) In regard to the variations of spraying employing various forms of the component materials whether in particle or rod form, applicant makes no argument that these limitations are unobvious per se without use of exothermically reacting powders.

Summary:

Claims rejected: 1 to 25, 47 and 48.

Claims allowed : None.

This rejection is made FINAL.

AG
A Golian:pc
(703) 557-3697

ALFRED L. LEAVITT
EXAMINER

E 780

RECEIVED

IN THE UNITED STATES PATENT OFFICE MAY 15 1968

GROUP 160

APPLICANTS : FERDINAND J. DITTRICH ET AL

SERIAL NO. : 592,238

FILED : MAY 26, 1966

FOR : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

GROUP : 160

May 8, 1968

HONORABLE COMMISSIONER OF PATENTS

WASHINGTON, D. C. 20231

REQUEST FOR EXTENSION OF TIME TO RESPOND TO OFFICE ACTION IN ACCORDANCE WITH RULE 136

S i r :

A Final Rejection was issued in the above-identified application on February 13, 1968, with a shortened period of time set to expire May 13, 1968.

An interview was had with the Examiner in charge of the above-identified application on May 6th, at which interview the merits of this application were discussed and, more particularly, the desirability of introducing further comparative data was discussed.

In order to permit time to obtain and submit this desirable comparative data, it is requested that the time for filing a response to the outstanding Action be extended for 30 days, to expire on June 12, 1968.

Request Granted May 15, 1968

Response DUE June 12, 1968

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By [signature]

Attorneys for Applicants

MGG:g

[signature]

ALFRED L. LEAVITT

EXAMINER

JUN 10 1968 U.S. PATENT OFFICE

E 781 Metco 305

RECEIVED JUN 12 1968 GROUP 160

IN THE UNITED STATES PATENT OFFICE

APPLICANTS : FERDINAND J. DITTRICH ET AL

SERIAL NO. : 592,238

FILED : MAY 26, 1966

FOR : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND

GROUP : 160

June 6, 1968

APPROVED JUN 13 1968 Director GROUP 160

HONORABLE COMMISSIONER OF PATENTS

WASHINGTON, D. C. 20231

SECOND REQUEST FOR EXTENSION OF TIME TO RESPOND TO OFFICE ACTION IN ACCORDANCE WITH RULE 136

S i r :

A Final Rejection has been issued in the above-identified application, dated February 13, 1968, setting a time for response to expire of May 13th.

As the result of an interview had with the Examiner in charge of this application, a request for extension of time to respond to the Final Rejection was filed in order to permit Applicants to run certain comparative tests and submit the data therefrom in affidavit form. These tests have now been completed and the affidavit has been prepared and forwarded to one of the Applicants for execution. This affidavit will be filed as soon as it is executed. However, it is anticipated that this will not be accomplished in time to have the Examiner consider such before the expiration of the period for response to the Final Rejection.

It is therefore requested that the period for response to the Final Rejection be extended for an additional thirty days, to expire on July 12, 1968, in order to permit the filing and consideration by the Examiner of this affidavit.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By Michael G. Sprung

MGG:g

E 783

RECEIVED
JUN 17 1968
GROUP 160

IN THE UNITED STATES PATENT OFFICE

APPLICANTS : FERDINAND J. DITTRICH ET AL

SERIAL NO. : 592,238

FILED : MAY 26, 1966

FOR : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND

GROUP : 160

June 10, 1968

THE HONORABLE COMMISSIONER OF PATENTS

WASHINGTON, D. C. 20231

RESPONSE TO FINAL REJECTION

S i r :

In response to the Final Rejection dated February [illegible], 1968, kindly amend the claims of the above-identified application as follows:

Claim 1, line 6, after "two", insert --distinct, unalloyed--

Line 7, change "which" to --in proximity and--

form sufficient to--

REMARKS

Reconsideration of the subject application is requested.

Applicants wish to thank the Examiner for courtesies shown their representative at a recent conference. The results of this conference are reflected in the amendments made hereto to claim 1 of the instant application and the following discussion.

Claim 1 has been amended to indicate that the components of the heat fusible materials are distinct and unalloyed with respect to each other and that they are present in the form

and in proportion such that they react exothermically with each other. These amendments are intended to more clearly point out the distinction between the heat fusible material of the process claimed herein and a mere physical mixture or an alloy of the two metals forming the heat fusible material.

As was pointed out at the above-referred-to conference, the process of the instant invention requires the utilization of a two component heat fusible material in a flame spray process which two components react together exothermically during flame spraying. It has been determined, and it is clearly pointed out in the instant specification, that the nature of the physical association of the two components of the heat fusible material used in this process is critical. These two components cannot be present as a mere powder mixture nor can they be present as an alloy of the two components. The physical association of these two components must be more intimate than that of a mixed powder but not as "intimate" as an alloy.

In the instant specification it has been pointed out that clad articles in various forms, including the form of a cored wire is sufficient to enable the two components to react together exothermically during flame spraying. It is insufficient to produce a wire having a matrix holding discrete particles of the two components. That is, for example, a wire made up by mixing powdered nickel, powdered aluminum and polyethylene and extruding such in wire form, will not present an exothermically reacting heat fusible material within the scope of this invention. In this construction the aluminum and nickel, although in wire form, are not so intimately associated as to permit and sustain

an exothermic reaction therebetween.

The Examiner has rejected Applicants' claims on various grounds. However, it is believed that as a result of the above-referred-to conference it is clear that the basis for this rejection lies in the Shepard patent, and in particular in a combination of Examples 4 and 6 of this patent. Example 6 of the Shepard patent shows the production of wire from a mixture of polyethylene and the powder disclosed in Example 5. The Examiner's contention has been that if the composition of Example 4 were substituted for the composition of Example 5 in the wire of Example 6, there would be a flame sprayable wire which would meet Applicants' claims. It is most strongly urged that this is not true. As stated above, a wire formed of a nickel-aluminum alloy using a polyethylene matrix binder or of mixed powdered nickel and aluminum, using a polymerized matrix binder, will not meet the terms of the instant claims since this structure does not permit of or sustain an exothermic reaction between the nickel aluminum components of the wire.

It is urged that the remainder of the references which have been considered by the Examiner all fall far short of the disclosure of Shepard in so far as they are anticipatory with respect to the claims of this application. Similarly, nothing is contained in these other references which would even allude to the intimacy of mixture of the two components, a mixture of Applicants' claimed process sufficient to permit these components to exothermically react with respect to each other.

At best, the Examiner's position with respect to the Shepard patent, and with respect to the other references in the

there is a possibility of there being an inherent anticipation; that is to say, the Examiner considers disclosure of the Shepard patent to inherently teach a structure which is within the scope of claim 1 of the instant application. As pointed out above, this inherent anticipation theory is considered to be unwarranted and not valid since, as a matter of fact, the products and structure disclosed by Shepard are incapable of meeting the critical requirement of exothermic reactivity of the composition of claim 1 of this application.

As a result of the above-referred-to conference, certain comparative tests have been conducted and the results thereof, which completely bear out the compositions set forth in the above discussion, have been put in affidavit form. This affidavit has been forwarded to the Affiant for execution and will be filed as soon as such execution is complete.

In view of the above discussion, it is most strongly urged that the Examiner reconsider his final rejection, and upon such reconsideration, conclude that the claims of the instant application define allowable subject matter. It is therefore requested that the claims of this application be indicated to be allowable.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By Michael B. Sheen
Attorneys for Applicants

MGG:G

E 787

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON, D.C. 20231

Paper No. 11

In Reply Please Refer To The Following:

EXAMINER'S NAME		
A. Golian		
161	May 26, 1966	592,238
GR. ART UN.	FILING DATE	SERIAL NO.

FERDINAND J. DITTRICH ET AL.
APPLICANT

INVENTION

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

BURGESS, DINKLAGE AND SPRUNG
605 Third Avenue
New York, New York 10016

MAILED
AUG 26 1968
GROUP 160

A Golian:pc
(703) 557-3697

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents.

1. ☐ The communication filed _____ is informal for the reason(s) checked below and should be corrected.

APPLICANT IS GIVEN ONE MONTH FROM THE DATE OF THIS LETTER OR UNTIL THE EXPIRATION OF THE PERIOD FOR RESPONSE SET IN THE LAST OFFICE ACTION, WHICHEVER IS LONGER, WITHIN WHICH TO CORRECT THE INFORMALITY.

a. ☐ The amendment to claim(s) _____, filed _____, fails to comply with the provisions of rule 121 (b) (c) and is accordingly held to be non-responsive under sec. (c) of the rule.

A supplemental paper correcting the informal portions and complying with the rule is required.

b. ☐ The paper is unsigned. A duplicate paper or ratification, properly signed, is required.

c. ☐ The paper is signed by _____, who is not of record. A new power of attorney with a ratification, or a new paper signed by a person of record, is required.

d. ☐ The communication is presented on paper which will not provide a permanent copy. A permanent copy, or a request that a permanent copy be made by the Office at applicant's expense, is required. See M. P. E. P. 714.07.

2. ☐ This application is being forwarded to Abandoned Files Unit in view of:

a. ☐ The letter of express abandonment which is in compliance with rule 138.

b. ☐ Applicant's failure to file the proposed amendment of _____ within the period for response set in the Office action dated _____.

3. ☐ In accordance with applicant's request, THE SHORTENED STATURORY PERIOD FOR RESPONSE TO THE OFFICE ACTION DATED _____ IS EXTENDED FOR ONE MONTH.

No further extension will be granted unless approved by the Commissioner. Rule 136(b).

4. ☑ Prosecution on the merits is closed in this application and the Notice of Allowance or other appropriate communication will be sent in due course, in view of:

a. ☑ Applicant's communication filed June 14, 1968 and June 20, 1968.

b. ☐ Telephone interview with _____ on _____.

c. ☐ Personal interview held with _____ on _____.

5. ☐ Other

Alfred L. Leavitt

ALFRED L. LEAVITT
EXAMINER

PTOL-037 (2-68)

☆ GPO: 1968-291-929

E 788

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON, D.C. 20231

Paper No. C 2566

In Reply Please Refer To The Following:

EXAMINER'S NAME		
A. Golian		
161	May 26, 1966	592,238
GR. ART UN.	FILING DATE	SERIAL NO.

FERDINAND J. DITTRICH ET AL.
APPLICANT

INVENTION

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

BURGESS, DINKLAGE AND SPRUNG
605 Third Avenue
New York, New York 10016

Mailed

MAILED
SEP 25 1968
GROUP 160

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents

EXAMINER'S CHANGE AND/OR ADDITION TO THE APPLICATION RECORD UPON ALLOWANCE

This application is in condition for allowance. Changes and/or citation of references are specified below. Should this not be acceptable to applicant, an appropriate amendment may be proposed under Rule 312. To ensure consideration of such amendment, it should be submitted on or before the date of remitting the issue fee.

PROSECUTION ON THE MERITS IS CLOSED AND A NOTICE OF ALLOWANCE WILL BE MAILED IN DUE COURSE.

The changes and/or additions are as follows:

On page 1, before the first paragraph the following has been added:

Abstract

Method of coating a surface by flame spraying two or more components which will react with one another during the flame spraying to form an intermetallic compound.

On page 43, the last paragraph has been cancelled. See 847 O.G. 331.

A Golian:pc
(703) 557-3697

ALFRED L. LEAVITT
EXAMINER

PLEASE FURNISH YOUR ZIP CODE IN ALL CORRESPONDENCE

E1

E 789

#19

IN THE UNITED STATES PATENT OFFICE

APPLICANTS : FERDINAND J. DITTRICH ET AL

SERIAL NO. : 592,238

FILED : MAY 26, 1966

FOR : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

GROUP : 160

STATE OF NEW YORK)
) SS.:
COUNTY OF NASSAU)

I, FERDINAND J. DITTRICH, being first sworn, depose and say:

That I am one of the co-inventors of the above-identified patent application;

That I have carried out, or have had carried out under my direction, certain tests as set forth hereinbelow:

1. A wire made up of polyethylene, nickel-powder and aluminum powder was made up according to the disclosure of Example 6 of U. S. Patent 2,936,229. This wire had an aluminum to nickel ratio of 1:4.72. This wire was sprayed, by flame spraying, using a spray gun as set forth in Example 32a of the above-identified patent application.

The aluminum and nickel did not exothermically, or in any other way, react during spraying and the substrate onto which the wire was flame sprayed was found to have a coating of mixed, unreacted aluminum and nickel. This coating, as flame sprayed, had a very poor adherance to the substrate.

2. Following the procedure set forth in Example 31 of the above-identified patent application, various proportioned clad powders of aluminum and nickel were flame sprayed onto a smooth, clean, mild steel substrate surface. The aluminum and nickel particles had the following percentages of aluminum, and the resulting flame sprayed coating had the following tensile bond strengths:

% Al	Tensile bond strength, Psi
0	0
2.5	2250
5.0	3570
10.0	3610

3. Example 1a of the above-identified patent application was followed, using a nickel-clad aluminum powder having a proportion of 20% aluminum and 80% nickel. The flame sprayed coating on mild steel had a tensile bond strength of 2750 psi.

A wire having the same proportions of nickel and aluminum and made in a manner such as is set forth in the above-identified application was flame sprayed onto different steel substrates. The tensile bond strengths varied from about 2775 to 3150.

Ferdinand J. Dittrich

Sworn to before me this
10th day of June, 1968

Kenneth A. Kunz
Notary Public
KENNETH A. KUNZ
Notary Public, State of New York
No. 52-7384700
Qualified in Nassau & Suffolk County
Commission Expires March 30, 1970

E 791

JUN 20 1968

Mailed 3[illegible]
RECEIVED

IN THE UNITED STATES PATENT OFFICE JUN 20 1968 #15

APPLICANTS	:	FERDINAND J. DITTRICH ET AL
SERIAL NO.	:	592,238
FILED	:	MAY 26, 1966
FOR	:	FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND
Group	:	160

GROUP 1

June 19, 1968

AMENDMENT

HONORABLE COMMISSIONER OF PATENTS
WASHINGTON, D.C.

Sir:

Supplementary to the Response to the Final Rejection dated June 10, 1968, enclosed herewith is an Affidavit Under the Provisions of Rule 132. The data set forth in this affidavit show the differences between the process claimed herein and the processes disclosed in the most pertinent art cited by the Examiner. It is requested that the Examiner consider this application with the affidavit and, upon such consideration, find the claims herein to be allowable.

Respectfully submitted,
BURGESS, DINKLAGE & SPRUNG

By: Michael G. Gilman
Michael G. Gilman

Enc.

BOARD OF APPEALS

JUL 19 1968

E 792 Gup

etco 305.5 Att

JUL 12 1968 U.S. PATENT OFFICE

NOTICE OF APPEAL FROM THE PRIMARY EXAMINER TO THE BOARD OF APPEALS

In re application of: FERDINAND J. DITTRICH, et al.

July 11, 1968

Serial No.: 592,238

For: FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Filed: May 26, 1966

Group Art Unit: 161

APPEAL NO. 875 05 #16

To Commissioner of Patents

Sir:

Applicant hereby appeals to the Board of Appeals from the decision dated February 13, 1968 of the Primary Examiner finally rejecting claims 1 to 25, 47 and 48

The item(s) checked below are appropriate:

1. [X] An extension of time to respond to the final rejection was granted on May 15, 1968 for 1 month(s). and on June 13, 1968 for 1 month.

File Ordered 7-22 8/13

File Received 8/15

2. [X] A timely response to the final rejection has been filed, as provided in 841 O.G. 1411.

3. [X] Fee $50.00:

   [ ] Enclosed

   [ ] Not required *(Fee paid in prior appeal)*

   [X] Charge to Deposit Account No. 02-4740 *(One additional copy of this Notice enclosed herewith)*

Signature (Rule 191(b)).....

BURGESS, DINKLAGE & SPRUNG

By [signature] Attorneys for Applicant

Post Office Address *(to which correspondence is to be sent).*

605 Third Avenue

New York City, N.Y. 10016

As of JUL 18 1968 fee(s) were applied to

WB

E 793

PATENT OFFICE
NOV 25 1968
ISSUE & GAZETTE BRANCH
NOV 18 1968
U.S. PATENT OFFICE

Metc 305 C 2010
AS/uh

IN THE UNITED STATES PATENT OFFICE

Applicants	:	Ferdinand J. Dittrich et al.
Serial No.	:	592,238
Filed	:	May 26, 1966
For	:	FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES
Group	:	A. U. 161 -- Examiner : A. Golian

November 14, 1968

Honorable Commissioner of Patents
Washington D. C. 20231

AMENDMENT UNDER RULE 312

The following is an amendment offered to the application in accordance with Rule 312. Kindly amend claim 1 as follows:

1. ~~(three times amended)~~ In the flame spray process in which a heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in such condition out of said zone in finely divided form onto a substrate, the improvement which comprises passing the heat-fusible material into said zone in the form of a composite comprising at least two distinct, ~~[unalloyed]~~ components unalloyed together as a single alloy and in proportion and form sufficient to exothermically react with each other at the temperature developed in the heating zone, forming an intermetallic compound.

F1

REMARKS

The above amendment is offered to clarify claim 1 as amended and to avoid any misinterpretation of the claim as previously drafted.

The amendment was offered to distinguish from a single alloy powder, and it was obviously not intended to exclude composites in which one or both of the distinct components are themselves in alloyed form. Thus, for example, in the preferred embodiment where one distinct component is nickel and the other distinct component is aluminum, either or both of these components may be in alloyed form, provided they are not simply alloyed together as a single alloy. There are numerous examples where a metal component which reacts exothermically with the other component is in an alloyed form as, for example, nickel alloy in Example 32 (i) and with iron as described on page 8.

It is therefore respectfully requested that the amendment be entered under Rule 312.

Respectfully submitted,

BURGESS, DINKLAGE & SPRUNG

By: _____
Attorneys for the Applicants

E 795

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON, D.C. 20231

Paper No. 18

In Reply Please Refer To The Following:

EXAMINER'S NAME		
A.G.Golian		
161	May 26,1966	592,238
GR. ART UNIT	FILING DATE	SERIAL NO

Ferdinand J. Dittrich et al
APPLICANT

INVENTION
Flame Spraying Exothermically Reacting Intermetallic Compound Forming Composites

Burgess, Dinklage and Sprung
605 Thrid Avenue
New York, New York 10016

Mailed

MAILED
NOV 1968
GROUP 160

The amendment filed Nov. 18, 1968 under Rule 312 has been considered, and has been:

1. [XX] entered.
2. [ ] entered as directed to matters of form not affecting the scope of the invention (0.3311).
3. [ ] disapproved. A report appears below.
4. [ ] entered in part. A report appears below.

By Direction of the Commissioner

Joseph R. Liberman
Director, Group 160

Report:

E 796

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON, D.C. 20231

C 256[illegible]

Paper No. 19

In Reply Please Refer To The Following:

EXAMINER'S NAME	A. G. Golian	
161	May 26, 1966	592,238
GR. ART UN.	FILING DATE	SERIAL NO.

Ferdinand J. Dittrich et al
APPLICANT

INVENTION
FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

BURGESS, DINKLAGE AND SPRUNG
605 Third Avenue
New York, New York 10016

Mailed

MAILED
DEC 3 1968
GROUP 160

Please find below a communication from the EXAMINER in charge of this application.

Commissioner of Patents

EXAMINER'S CHANGE AND/OR ADDITION TO THE APPLICATION RECORD UPON ALLOWANCE

This application is in condition for allowance. Changes and/or citation of references are specified below. Should this not be acceptable to applicant, an appropriate amendment may be proposed under Rule 312. To ensure consideration of such amendment, it should be submitted on or before the date of remitting the issue fee.

PROSECUTION ON THE MERITS IS CLOSED AND A NOTICE OF ALLOWANCE WILL BE MAILED IN DUE COURSE.

The changes and/or additions are as follows:

The following has been substituted for the first paragraph in the specification. This is a division of application Serial No. 442,727, filed March 25, 1965, now Patent No. 3,322,515, which was a continuation-in-part of applications, Serial No. 72,543, filed November 22, 1960, now abandoned; Serial No. 134,544, filed August 16, 1961, now Patent No. 3,254,970; Serial No. 237,786, filed October 26, 1962, now abandoned; and Serial No. 343,705, filed February 10, 1964, now abandoned.

(6-65)

E 797

ADDRESS ONLY
THE COMMISSIONER OF PATENTS
WASHINGTON, D. C. 20231

U. S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON

All communications regarding this application should give the serial number, date of filing, and name of the applicant.

NOTICE OF ALLOWANCE AND ISSUE FEE DUE

The application for patent identified below has been examined and found allowable for issuance of Letters Patent.

	FILING DATE	SERIAL NO.	NO. OF CLAIMS ALLOWED	EXAMINER	GROUP
	05/26/66	592238	27	Leavitt	161
APPLICANT	Dittrich, Ferdinand J.; Bellmore, and Shepard, Arthur P.; Flushing, N. Y.			MAILED Oct. 29, 1968 mjb	
TITLE OF INVENTION (X indicates as amended by examiner)	Flame spraying exothermically reacting intermetallic compound forming composites				
	DRAWING NO. SHEETS @ $2 EACH: 001	SPEC NO. PAGES @ $10 EACH: 10	ISSUE FEE DUE: $202	CLASS-SUB: 117/105.	

With the allowance of the application, the above indicated Issue Fee becomes due and payment must be made within three months of the date of this Notice or the application shall be regarded as abandoned.

The Issue Fee is one hundred dollars ($100) plus two dollars ($2) for each printed sheet of drawing and ten dollars ($10) for each printed page of specification, or portion thereof.

Inasmuch as the number of printed pages of specification must be determined in advance of printing from the amount of matter in the allowed application, the Issue Fee is subject to change. After the patent has been printed, the estimate will be reviewed in light of the actual number of pages of specification. If it is found that an overcharge was made, you will be notified thereof with the issuance of the Patent and the matter will be referred to the Finance Branch for appropriate action. If the number of pages is underestimated by two or more pages, you will receive a notice of Additional Issue Fee Due with the Patent and payment of this amount must be made within three months of the date of that Notice. Failure to remit any additional fee due within three months from the date of that Notice will result in lapse of the Patent.

As a convenience in remitting this fee, use of the enclosed Form POL-85a is suggested. The Issue Fee will not be received from anyone other than the applicant, his assignee or attorney, or a party in interest as shown by the records of the Patent Office. A form is enclosed relating to the address of the inventor(s) which requires your attention.

If it is desired to have the patent issued to an assignee or assignees, an assignment, together with the fee for recording the same, must be filed in this Office on or before the date of payment of the Issue Fee.

The patent will be issued and forwarded within approximately two months after receipt of the Issue Fee.

By direction of the Commissioner.

Burgess, Dinklage, et al
605 Third Ave.
New York, N. Y. 10016

MAIL ROOM
DEC 23 1968
PATENT OFFICE

E 798

#2

NT-SPP

Metco 305.5 Div.

PATENT OFFICE
FEB 5 1969
ISSUE & GAZETTE BRANCH

IN THE UNITED STATES PATENT OFFICE

Applicants: FERDINAND J. DITTRICH, et al

Serial No.: 592,238

Filed: May 26, 1966 Group 161

For: FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

SUPPLEMENTAL DECLARATION

We, the undersigned, declare with respect to the above-entitled application that the subject matter of the allowed claims was part of our invention, was invented before we filed our original application, above-identified, for such invention; that we do not know and do not believe that the same was ever known or used before our invention thereof, or patented or described in any printed publication in any country before our invention thereof, or more than one year before our application, or in public use or on sale in the United States more than one year before the date of our application, that said invention has not been patented in any foreign country before the date of our application on an application filed by us or our legal representatives or assigns more than 12 months prior to our application in the United States, and has not been abandoned.

The undersigned petitioners declare further that all statements made herein of their own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: 18 Dec 1968 Inventor: Ferdinand J Dittrich (Signature)

Ferdinand J. Dittrich (sign exactly as typed)

Date: _____ Inventor: _____ (Signature)

Arthur P. Shepard (sign exactly as typed)

Date: Dec. 12, 1968 Inventor: Arthur P Shepard (Signature)

(sign exactly as typed)

Date: _____ Inventor: _____ (Signature)

(sign exactly as typed)

E 799

U. S. Department of Commerce
Patent Office

FOR FEE TRANSMITTAL

Form to the Patent Office. When properly completed it may be used to pay

[illegible] pendency will note and will be issued numbered 1 thru 5 below. The Issue Fee Receipt, in all cases, will be

[illegible] in box at lower left of this form. If desired, use the reverse side of your Notice of Allowance for matter

copy [illegible] form.

1. The COMMISSIONER OF PATENTS is requested to apply the accompanying fee to the case identified below, and deliver the patent as

addressed.

BURGESS, DINKLAGE & SPRUNG

By: [signature]
Attorney, Agent or Applicant

Dec. 19, 1968
Date

NOTE – Issue Fees will not be received from other than the applicant, his assignee, or attorney, or a party in interest as shown by the records of the Patent Office. Issue Fees will not be applied to pending applications.

	FILING DATE	SERIAL NO.	NO. OF CLAIMS ALLOWED	EXAMINER
	5/26/66	597238	27	Leavitt
APPLICANT	[illegible], Ferdinand J.; Bellmore, and Shepard, Arthur P.; Fleming, [illegible] Y.			MAILED Oct. 29, 1968
TITLE OF INVENTION (If indicated as amended by examiner)	Plasma [illegible] chemically [illegible] intermetallic compound forming composites			NOTICE OF ALLOWANCE DATE
	NO. SHEETS @ $2 EACH	NO. PAGES @ $10 EACH	ISSUE FEE DUE	CLASS-SUB
	1	10	$202	117/105. 4

2. Assignment

As of JAN 8 1969

METCO INC.

Fee Code(s) 1043 100.00
107 100.00
1085 2.00

3. FEE ENCLOSED

Patent Office

$202.00

(Authorized Signature)

RETURN TO [illegible]
APPROVED FOR [illegible]

MAILING INSTRUCTIONS

NOTE – The office will send the patent to the address entered in stub at left below unless you direct otherwise. Use the spaces provided to indicate any changes which affect the delivery of the patent. However, if an additional Issue Fee Due Notice is required, this notice is cancelled and the patent will be mailed to the address entered in the stub at left below.

CREDIT APPLIED

4. Do not send the patent to the addressee listed below. Send patent to (check one)

CODE(S) 10.00 $10.00

☐ Practitioner

☐ Assignee

☐ Associate Attorney (See specific authorization in file)

☐ Change of address – Attorney

DATE MAR 26 1969

The address of the person checked above is typed in Item 5 below.

Charged to Account No.

5. (If an additional Issue Fee is required the patent will not be sent to this address – PLEASE FURNISH ZIP CODE)

( ) Supplemental Declaration

( ) Priority is hereby claimed on the bas

Country Serial No.

Respectfully,

BURGESS, DINKLAGE & SPRUNG

By [signature]

E 800

Form PDL-367

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE

PAT[illegible] NUMBER
3436280

DATE OF THIS NOTICE
April 1, 1969

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#21

IN THE UNITED STATES PATENT OFFICE

APPLICANTS : FERDINAND J. DITTRICH, et al

SERIAL NO. : 592,238

FILED : MAY 26, 1966

FOR : FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

GROUP : 161

PATENT NO. : 3,436,248 ISSUED: April 1, 1969

April 23, 1969

HONORABLE COMMISSIONER OF PATENTS

WASHINGTON, D.C. 20231

as indicated

APPLICATION FOR CERTIFICATE OF CORRECTION

S i r :

Applicants and heir Assignee of the above entitled application and patent issued thereon respectfully show as follows:

I. The above application issued to patent No. 3,436,248 on April 1, 1969.

II. Column 9, line 38 (specification, page 23, line 22) "Al-Nn" should be --Al-Ni--;

III. Column 13, line 56 (specification, page 36, 2nd last line) "poyder" should be --powder--;

IV. Column 14, line 20 (specification, page 38, line 13) "end" should be --and--.

V. Column 15, first column, line 58 (specification, page 42, line 5, 2nd column) "B Co" should be --B Ca--;

VII. Column 15, line 33, 2nd Column (specification page 42, line 24, 3rd column) "Ce Nb" should be --Ge Nb--;

VIII. Column 15, line 34, 2nd Column (specification, page 42, line 25, 3rd column) "Ce Zr" should be --Ge Zr--;

IX. Column 15, line 35, 2nd column (specification, page 42, line 24, 3rd column) "H V" should be canceled.

X. Column 15, line 42, 2nd column (specification, page 42, line 6, 4th column) " K Te" should be --K Tl--;

XI. Column 15, line 46, 2nd column (specification, page 42, 4th column, line 10) "La Te" should be --La Tl--;

XII. Column ~~15~~ 18, line 24 (Official Action dated 12-11-52) "Mackin et al" should read --Mackiw et al --.

XIII. The mistakes complained of were incurred through the fault of the Patent Office and without any fait whatsoever on the part of the said applicants or their assignee, as clearly disclosed by the files and records of the Patent Office.

XIV. The original deed of the said patent is returned herewith.

WHEREFORE, the said applicants and their assignee pray that a Certificate of Correction duly issue and be endorsed upon said Letters Patent and recorded in the records of patents, stating the fact and nature of said mistake herein complained of, and that a printed copy of such Certificate be attached to each printed copy of the specification.

Respectfully submitted,
BURGESS DINKLAGE & SPRUNG

By M. F. Sprung

Encl.

E 803

U.S. DEPARTMENT OF COMMERCE
PATENT OFFICE
WASHINGTON, D.C. 20231

#22

U. S. PATENT OFFICE
COMMISSIONER'S OFFICE
DEC 1 1969

COPY MAILED

Re: Patent No. 3,436,248 :
Ferdinand J. Dittrich, et al. :
Issued Apr. 1, 1969 :
For: Flame Spraying Exothermically Reacting Intermetallic Compound Forming Composites : Request for Certificate of Correction

Consideration has been given your request for the issuance of a certificate of correction in the above-identified patent.

With respect to the alleged errors in column 15, first column, line 58; column 15, lines 35, 42 and 46; second column, inspection of the application for the patent reveals that the patent is printed in accordance with the record in the Patent Office of the application as passed to issue by the Examiner. Therefore, no correction is in order here, under Rule 322.

A certificate of correction will be issued to correct the remaining errors listed in your request.

Further, with respect to the alleged error in column 15, line 24, said error occurs in column 18, line 24 and the certificate will so indicate.

FOR THE COMMISSIONER:
S. WM. COCHRAN, Acting Solicitor

Burgess, Dinklage & Sprung
605 Third Avenue
New York, N. Y. 10016

By: [signature]
Law Examiner

MNG

PX-7

E 804

UNITED STATES DISTRICT COURT
EASTERN DISTRICT OF NEW YORK

EUTECTIC CORPORATION, NEW METALS CORPORATION, and METALLIZING CO. OF AMERICA, INC., Plaintiffs,	Civil Action No. 72 Civ. 102 (ERN)
v.	
METCO, INC., Defendant.	

PATENTS IN SUIT AND PRIOR ART

SANDOE, HOPGOOD & CALIMAFDE

LINCOLN BUILDING

60 EAST 42ND STREET

NEW YORK, N.Y.

E 805

May 30, 1967 F. J. DITTRICH ETAL 3,322,515

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Filed March 25, 1965

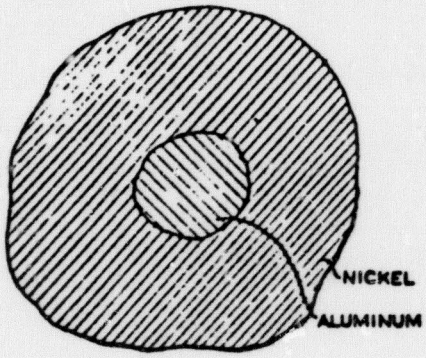

Fig. 1

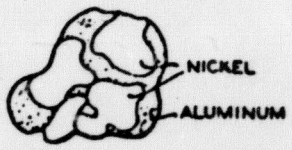

Fig. 2

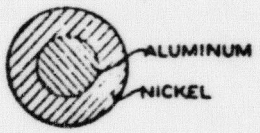

Fig. 3

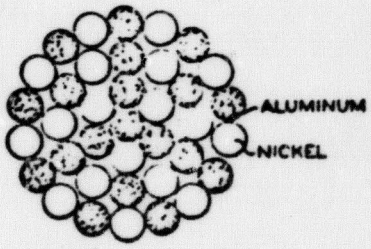

Fig. 4

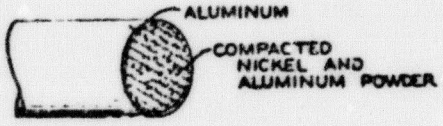

Fig. 5

INVENTORS

FERDINAND J. DITTRICH

ARTHUR P. SHEPARD

BY Burgess, Dinklage & Sprung

ATTORNEYS

E 806

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,322,515 May 30, 1967

Ferdinand J. Dittrich et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 49, strike out "the", second occurrence; column 7, line 5, for "as" read -- at --; line 7, for "deposite" read -- deposit --; line 69, for "aluminum" read -- alumina --; column 9, line 6, for "sprayer" read -- sprayed --; column 16, line 75, for "reactiing" read -- reacting --.

Signed and sealed this 5th day of December 1967.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents

United States Patent Office E 807 3,322,515
Patented May 30, 1967

3,322,515

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Ferdinand J. Dittrich, Bellmore, and Arthur P. Shepard, Flushing, N.Y., assignors to Metco, Inc., a corporation of New Jersey

Filed Mar. 25, 1965, Ser. No. 442,727
28 Claims. (Cl. 29—191.2)

This is a continuation-in-part of copending applications, Ser. No. 72,543, filed Nov. 22, 1960, now abandoned; Ser. No. 134,544, filed Aug. 16, 1961, now Patent No. 3,254,970; Ser. No. 237,786, filed Oct. 26, 1962, now abandoned; and Ser. No. 343,705, filed Feb. 10, 1964.

This invention relates to the flame spraying of exothermically reacting intermetallic compound forming composites. The invention more particularly relates to the flame spraying of flame spray materials in the form of composites containing two or more components which will exothermically react with each other during the spraying, forming one or more intermetallic compounds, and to a novel group of such composites including powders and wires.

Flame spraying involves the feeding of a heat-fusible material into a heating zone, wherein the same is melted or at least heat-softened, and then propelled from the heating zone in a finely divided form, generally onto a surface to be coated.

The material being sprayed is generally fed into the heating zone in the form of either a powder or a wire (the latter term designating both rods and wires). The spraying is effected in a device known as a heat-fusible material spray gun or a flame spray gun.

In the wire type flame spray gun the rod or wire of the material to be sprayed is fed into the heating zone formed by a flame of some type, where it is melted or at least heat-softened and atomized, usually by blast gas, and thence propelled in finely divided form onto the surface to be coated. The rod or wire may be a conventionally formed rod or wire of a metal, or may be formed by sintering together finely divided material, or by bonding together finely divided material by means of a plastic binder or other suitable binder which disintegrates in the heat of the heating zone, thereby releasing the material to be sprayed in finely divided form.

For spraying finely divided, i.e., powdered material, a powder type flame spray gun is used in which the powder, usually entrained in a carrier gas, is fed into the heating zone of the gun formed by a flame of some type. The powder is either melted or at least the surface of the grains heat-softened in this zone, and the thus thermally conditioned particles propelled onto a surface to provide a coating. In the powder type spray gun as no "atomizing" energy is required, a separate blast gas is often dispensed with, though the same may be supplied in order to aid in accelerating the particles and propelling them toward the surface to be coated.

The blast gas may be provided for both the wire type and powder type guns to perform the additional function of cooling the workpiece and the coating being formed thereon.

The heat for the heating zone is most commonly produced from a flame caused by the combustion of a fuel, such as acetylene, propane, natural gas, or the like, using oxygen or air as the oxidizing agent. The heat may, however, also be produced by an electrical arc flame or, in the newer type of guns, by a plasma flame. The plasma flame may in itself constitute part of an electric arc, or, in accordance with a newer development, may be in the form of a "free plasma stream," i.e., a stream of plasma

which may be considered independent of the arc as it does not contribute to the electric flow between electrodes.

Heat-fusible material spray guns utilizing electric resistance heating or induction heating as the heat source have also been proposed but have not proven commercially successful except in connection with the spraying of low melting point metals, such as solders, lead and zinc.

Flame spraying in the initial stages of its commercial development was used mostly for the spraying of various metals and was often referred to as metallizing. However, the art of flame spraying extends to the spraying of a much wider group of materials, including higher melting point or refractory metals, ceramics, cermets, and the like, and such materials are of increasing commercial interest.

In the case of spraying heat-fusible materials in the initial form of a rod or wire, the rod or wire is generally of a single composition, i.e., in the form of a specific metal, alloy, ceramic, or the like. While it is true that rods or wires formed from finely divided material bound together with a binder of plastic or the like, as mentioned above, were known, the binder generally did not take part in the spraying or contribute to the coating, and merely served the purpose of maintaining the rod or wire in shape until fed into the heating zone.

In the case of flame spray powders, while powders formed of several constituents were known, the same were generally in the form of a powder mixture of the individual constituents or, at best, a particle aggregate.

One object of this invention is the spraying of the heat-fusible material in a novel form which allows the obtaining of superior results.

A further object of this invention is a novel group of flame spray materials.

These and still further objects will become apparent from the following description read in conjunction with the drawing in which:

FIG. 1 diagrammatically shows a cross-section of a grain of novel powder in accordance with the invention;

FIG. 2 is a cross-section of a further embodiment of an aggregate grain of novel flame spray powder in accordance with the invention;

FIG. 3 is a diagrammatic cross-section of an embodiment of a novel flame spray wire in accordance with the invention;

FIG. 4 shows a cross-section of a further embodiment of a novel flame spray wire in accordance with the invention: and

FIG. 5 shows a still further embodiment of a novel flame spray wire in accordance with the invention.

In accordance with the invention, the flame spraying is effected with the heat-fusible material in the form of a composite containing at least two components which will exothermically react with each other at the temperatures developed during the spraying, forming an intermetallic compound.

The term "composite" as used herein is intended to designate a structurally integral unit and does not include a mere mixture of components which may be physically separated without any destruction of the structure. Thus, in the case of powder, the term "composite" does not include a simple mixture of individual granules of the separate components, but requires that each of the individual granules contain the separate components which will exothermically react, forming intermetallic compounds. In the case of wire, the individual components must be incorporated in a single wire. In the composite the components must be in intimate contact with each other.

In connection with powders, each grain may consist of an aggregate containing the two components which

will exothermically react, forming the intermetallic compound, but preferably the individual grains of the powder are in the form of a clad composite consisting of a nucleus of one of the components and at least one coating layer of the other component. Alternatively, the composite may consist of separate, concentric coating layers of the two components and a nucleus of still a third material.

In the case of wires, the composites may be in the form of a wire having a coating sheath of one material and a core of the other, alternate coating sheaths of the components and a core of a third material, a wire formed by twisting or rolling separate wire strands of the components, a wire consisting of a sheath of one component and a core containing the other component in powder or compacted form, a wire consisting of a sheath of one component and a core containing a compacted powder mixture of this same component material and one or more other components, a wire consisting of a plastic sheath and a core containing a compacted powder mixture of components, etc.

In order for the wires to be satisfactory for spraying, the same must not cavitate at the tip when heated, and should preferably be capable of forming a pointed or slightly tapered tip when being melted and sprayed. Thus, if the wires have an outer layer or sheath of one component and an inner core of another component, the inner core cannot have a lower melting point than the outer sheath, as otherwise the inner core will initially melt, causing cavitation at the tip. For example, if the wire is composed of nickel and aluminum as the exothermically reacting components and is in the form of a core with a coating sheath, the core must be nickel and the coating sheath aluminum, as otherwise during the spraying the core will initially melt out, causing the cavitation which will interfere with a satisfactory spraying operation. The wire having the melting-point characteristics so as to allow the melting off of the tip without this cavitation, is referred to herein and in the claims as "non-cavitating wire."

As the components, any two metallics which may be melted together to form an intermetallic compound in an exothermic reaction may be used. The components should release about 3000 calories per gram atom, and preferably at least 7500 calories per gram atom in the exothermic reaction forming the intermetallic compounds. The term "calories per gram atom" as used herein denotes the number of gram calories which the average atomic weight in the grams of the intermetallic compound formed will generate in so being formed. While the components are preferably present in the stoichiometric proportions required for the formation of the intermetallic compound, it is, however, possible to also have an excess of one or the other provided the relative amounts are sufficient to release the quantities of heat indicated above in the formation of the intermetallic compounds.

An extremely large number of metal components are known which can be melted together in an exothermic reaction, forming an intermetallic compound with the generation of heat. Any of these component pairs may be utilized in accordance with the invention, it only being required that the same be capable of being initially formed into the composite suitable for spraying and that the intermetallic compounds formed therefrom liberate the required amount of heat in the intermetallic compounds-formation and are suitable as components of a sprayed coating. As a general rule, components which will form intermetallic compounds having a higher melting point will liberate sufficient heat to be useful in accordance with the invention. In certain instances, however, components which will form intermetallic compounds which do not have as high a melting point, will also liberate sufficient heat in the exothermic reaction and thus be useful. Preferred components are aluminum with at least one of Co, Cr, Mo, W, Ta, Nb, Ti, or most preferably Ni; or silicon with at least one of Ti, Nb, Cr, W, Co, Mo, Ni or Ta.

While iron itself is not a satisfactory component, the same may be present in addition to another component, which in itself is satisfactory, such as in the form of an alloy therewith. This other component, however, must be present in amount sufficient to form the intermetallic compound with the other component of the composite, with the generation of sufficient heat to aid the spraying operation. Thus, for example, iron which just contains enough alloyed nickel to render the same rust-resistant, does not contain enough nickel for an effective exothermic reaction with aluminum. Generally an alloy if nickel and iron must contain at least about 12% nickel for this purpose.

FIG. 1 shows a composite powder consisting of a nucleus of aluminum and a coating layer of nickel. FIG. 2 shows an aggregate of these components; and FIGS. 3, 4, and 5 show various forms of wire containing these components, FIG. 3 showing a wire having an aluminum core with a nickel sheath. FIG. 4 showing a wire made of alternate strands of nickel and aluminum wire, as for example 18 strands of 25 gauge (.019" diameter) nickel wire, and 19 strands of 25 gauge aluminum wire; and FIG. 5 shows a sheath of aluminum filled with granules of nickel and aluminum.

Where one of the component metals is available as a metal hydride, the same may be used in this form rather than as a metal per se. When flame sprayed the hydrogen gas evolved from the hydride produces a reducing atmosphere, which in turn suppresses oxidation of the intermetallic compounds during and immediately after their formation. Thus, for example, in place of titanium, titanium hydride may be used as one of the components.

Also for the purpose of reducing oxidation a metal hydride, such as titanium hydride, may be added in a minor amount to the other components. Thus, for example, 1–10% by weight, and preferably 1–5% by weight, based on the total of the hydride and other components, may be used.

In addition, the powder granules and the wire may contain other conventional flame spray components, or be sprayed in admixture or in conjunction therewith. Thus, for example, the coated powders may additionally contain other coating layers of other flame spray components or may contain a nucleus of another flame spray material with alternate coating layers of the components which will exothermically react, forming the intermetallic. In a similar manner, the aggregates or the wires may contain further flame spray components, and in the case of powders, the same may additionally be admixed with any other desired flame spray powder.

The clad powders, in accordance with the invention, may be formed in any known or desired manner, and preferably by the known chemical plating processes, in which coating material is deposited on a seed or nucleus of another material, or in which multiple layers of various materials are built up on the seed material or in which various materials are co-deposited in a single layer on the seed material.

A mode of forming the clad powders involves the depositing of a metal from a solution by reduction on a seed or nucleus, such as by the hydrogen reduction of ammoniacal solutions of nickel and ammonium sulfate on a seed powder catalyzed by the addition of anthraquinone. It is also possible to form the coating by the use of other known coating processes, such as coating by vapor deposition, by the thermal decomposition of metal carbonyls, by hydrogen reduction of metal halide vapors, by thermal deposition of halides, hydrides, carbonyls, organometals, or other volatile compounds, or by displacement gas plating and the like.

A preferred and greatly simplified mode of forming the clad powders in accordance with the invention is the depositing of one component as a coating in the form of a paint on the other component. Thus, one of the components which is to form the coating or cladding, may be dispersed in finely divided form in a binder or lacquer so as, in effect, to form a paint in which this component corresponds to the pigment. The paint is then used to coat core particles of the other component and the binder or lacquer allowed to set or dry. The binder material is preferably a resin which does not depend on solvent evaporation in order to form a dried or set film, and which film will decompose or break down in the heat of the spraying process. The binder, for example, may be a phenolic varnish or any other known or conventional varnish, preferably containing a resin as the varnish solids. The component which is initially mixed with the binder or varnish should preferably be as finely divided as possible, as for example —325 mesh. The other component which constitutes the core should be approximately or only slightly below the particle size ultimately desired for the spray powder. The coating of the core component with the "paint" may be effected in any known or desired manner, and it is simply necessary to mix the two materials together and allow the binder to dry or set, which will result in a fairly free-flowing powder consisting of the core component coated with a cladding of the other component bound in the binder.

The aggregates may be formed by compacting or briquetting the various components into the individual granules, or into larger aggregates and then breaking these aggregates into the granules.

The wires may be formed in the known conventional manner for forming wires with various components as, for example, by shrinking a sheath on a core, by forming the core with powder, by twisting the component wires, followed by rolling, drawing, swaging, or the like if desired.

In accordance with one mode of manufacture, one of the components may be formed into a tube or sheath and filled with a powder of the other component or a powder comprising a mixture of the two components, or containing additional components. The tube ends are then sealed and the wire reduced to the desired wire diameter by swaging, rolling or drawing. Preferably the powder or powder mixture is first compressed into cylindrical briquettes before being placed in the sheath or core. The sealing of the tube ends after loading with the powder or powder mixture can be effected, for instance, by insertion of a plug, for example of the metal of the sheath, by welding, twisting, crimping, or the like.

Powders in accordance with the invention should have the general over-all shape and size of conventional, flame-spray powders, and thus for example should have a size between —60 mesh and +3 microns and preferably —140 mesh and +10 microns (U.S. Standard screen mesh size). Most preferably the powder should be as uniform as possible in grain size, with the individual grains not varying by more than 250 microns and preferably 75 microns.

Depending on the particular flame spray process and the desired purpose, the composite powders may be sprayed per se or in combination with other different composite powders, or in combination with other conventional flame spray powders or powder components.

While the powders are preferably sprayed, as such, in a powder-type of flame spray gun, it is also possible to combine the same in the form of a wire or rod, using a plastic or similar binder, which decomposes in the heating zone of the gun, or in certain cases the powders may be compacted and/or sintered together in the form of a rod or wire. The wires must have the conventional sizes and accuracy tolerances for flame spray wires, and thus for example may vary in size between ¼" and 20 gauge, and are preferably of the following sizes: 3/16" +.0005" to —.0025", ⅛" +.0005" to —.0025", 11 gauge +.0005" to —.0025", and 15 gauge +.001", with a smooth, clean finish free from surface marks, blemishes, or defects. The wires are sprayed in the conventional manner, using conventional wire-type flame spray guns.

In combining, in the exothermic reaction, forming the intermetallic compound, the components generate heat in situ in the actual material which is to form at least a part of the coating. This is to be distinguished from flame-spray processes and materials in which heat is generated by a reaction, such as an oxidation reaction, in which a foreign and non-metallic element is introduced and in which undesirable components may be produced. Aside from greatly contributing to the thermal efficiency of the process, the heat generated in situ in the formation of the intermetallic compound produces novel results, in many instances forming a denser, more adhering coating, having characteristics of at least a partially fused coating. In many instances the coating has self-bonding characteristics, so that special surface preparation, other than a good cleaning, is not required. The spraying in all other respects is effected in the conventional, well-known manner, using conventional flame spray equipment, and the conventional surface preparation may be utilized, if desired. The composites in accordance with the invention may be sprayed in conjunction with, or in addition to, other flame spray materials conventionally used in the art, or may be sprayed in combination or conjunction with the others.

The use of the composites as, for example, the nickel-aluminum composites, will generally improve the bond of the total sprayed material, and thus of the other component or components to the substrate, sometimes making the mixture self-bonding. The particle bond will be improved and the coating will be denser, so that its porosity may be decreased. In general, as little as 10% by weight of the composites in accordance with the invention will be sufficient to substantially improve the bonding characteristics and decrease the porosity of other flame spray materials, such as conventional flame spray metals, alloys or ceramics. There is, of course, no upper limit on the amount, as the composite may be sprayed per se, but generally at least about 20% by weight of the other component is required if this component is to have a pronounced effect on the characteristics of the coating.

The following examples are given by way of illustration and not limitation:

Example 1

(a) An aluminum powder having a particle size between —140 mesh and +325 mesh (U.S. Standard screen size) is coated with nickel in the known manner by the hydrogen reduction of an ammoniacal solution of nickel and ammonium sulphate, using anthraquinone as the coating catalyst. The reduction is effected at a temperature between about 300 and 350° F. in a mechanically agitated autoclave using solutions containing 40–50 grams per liter of nickel and 10–400 grams per liter of $(NH_4)_2SO_4$ and 20–30 grams per liter of NH_3. About .2 gram per liter of anthraquinone is used as the catalyst and the autoclave is pressurized with hydrogen at a pressure of about 300 lbs. p.s.i. After the nickel solution is depleted and the aluminum coated with an initial coating of nickel, the solution is discharged from the autoclave and replenished with a fresh solution which need not contain further amounts of the anthraquinone coating catalyst, as the initially formed nickel coating in itself acts as a catalyst. The cycle is continuously repeated until a composite powder is formed containing about 16 to 18% by weight aluminum and 84 to 82% by weight of nickel, and a size of —100 to +270 mesh.

The powder thus formed is flame-sprayed on a mild steel plate which has been surface-cleaned with emery cloth. The spraying is effected at about 9 inches from the plate, using a powder-type flame-spray gun as described

in U.S. Patent 2,961,335, issued Nov. 22, 1960, and sold by Metco Inc. of Westbury, Long Island, under the trade name of "Thermospray" powder gun. The spraying is effected at a rate of 6 to 9 lbs. of powder per hour, using acetylene gas as the fuel as a pressure of 10 p.s.i. and a flow rate of 17 to 25 cu. ft./hr. and oxygen as the oxidizing gas at a pressure of 12 p.s.i. and a flow rate of 29 to 35 cu. ft. hr.

The nickel coating and the aluminum base combine in the heat of the flame with a strong exothermic action, forming a mixture of nickel aluminum intermetallic compounds which deposite on the base as a dense, high quality coating which exhibits self-bonding characteristics. A coating layer of .002"–.004" thickness is built up in this manner. The coating may be used as a base material for spraying of further layers of different metals or the like, and serves as an excellent intermediate bonding layer.

The coating layer may also be built up to a greater thickness as, for example, .010"–.020", for use as an oxygen barrier undercoat, or to even greater thickness as, for example, .020"–.040" or thicker as a wear-resistant–oxidation-resistant surface.

Due to its self-bonding characteristics the sprayed coating will adhere to a base without the conventional surface preparation or roughening, and due to the natural characteristics of a sprayed material, will allow further materials to be sprayed thereon with good bonding. The coating formed from the powder has excellent oxidation-resistant characteristics even at high temperatures and in oxidizing atmospheres, and will for example prevent the oxidation of base materials, such as molybdenum or the like. The sprayed coatings may be used as a lining in metal-melting crucibles or molten metal-handling equipment, and will not be wetted or penetrated by many molten metals, including self-fluxing alloys. Coatings formed of the sprayed material also show good potential as high temperature, wear-resistant coatings.

When the example is repeated on a molybdenum rod of 3/16" diameter, with a coating between .010"–.012" thick, the coated rod may be repeatedly heated to approximately 2000° F. in air, in an electric furnace and cooled to room temperature with no visible oxidation occurring.

Similar results may also be obtained if the composite powder contains 10–45% by weight of aluminum and 55–90% by weight of nickel.

(b) Example 1(a) is repeated, using, however, cobalt in place of the nickel. Comparable results are obtained.

(c) Example 1(a) is repeated, using titanium hydride (TiH_2) powder in place of the aluminum and in an amount of 25–85 weight percent, and preferably 60–85 weight percent of the total. The coating formed upon spraying is hard and dense, and when sprayed on a smooth, pressed and sintered Al_2O_3 substrate, an excellent bond is formed. The spraying may be effected with an oxygen-hydrogen or oxygen-acetylene flame.

Example 2

Example 1 is repeated with the spraying being effected in turn on the following bases and prepared in the following manner:

Low alloy steels and stainless steels, smooth-ground to remove surface contamination; copper and copper base alloys, rough-ground or light-grit-blasted; aluminum and aluminum base alloys, rough-ground or light-grit-blasted; magnesium, rough-ground or light-grit-blasted; and titanium, rough-ground or light-grit-blasted.

In each case when a further material, such as steel, aluminum or the like, was sprayed over the coating in the conventional and well known manner, the same was bonded with a tenacious bond, though if this material had been initially sprayed on the surface as prepared in the manner indicated above, a satisfactory bond would not be obtained.

Example 3

The nickel-clad powder of Example 1 is mixed with an Al_2O_3 powder having a particle size between 62 microns and 10 microns, in the ratio of about 40% of the nickel-clad powder with 60% by weight of the ceramic. The powder is sprayed, using the gun described in Example 1, on a mild steel plate which has been surface-cleared by smooth grinding. Spraying is effected at a distance of about 9" from the plate at a rate of about 4 to 8 lbs. of powder per hr., using acetylene at a pressure of 10 lbs. p.s.i. and a flow rate of 17–25 cu. ft./hr., and oxygen at a pressure of 12 p.s.i. and a flow rate of 29–35 cu. ft./hr.

A self-bonding cermet coating is formed which showed excellent thermal shock-resistance, hardness, abrasion-resistance, and which strongly inhibited oxidation of the base.

It is possible to vary the percentages of the ceramic in the mixture between 5 and 85% in order to vary the properties of the coating. With an increased amount of the intermetallic compound in the cermet coating formed, the bonding and thermal shock-resistant properties increased, whereas with an increased amount of the ceramic, the hardness and wear-resistant properties of the coating are increased and the thermal conductivity decreased.

Example 4

Example 3 is repeated, using the following materials in place of the aluminum oxide:

Zirconia, calcium zirconate, magnesium zirconate, spinel, ceric oxide, hafnium oxide, rare earth oxides, molybdenum disilicide, tungsten silicide, chromium silicide, titanium silicide, tungsten carbide, titanium carbide and chromium carbide.

In each case an excellent coating was formed.

Example 5

A nucleus of silicon powder is coated with nickel to form a nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 75–85% nickel based on the silicon-nickel total. The composite powder is sprayed with the flame spray gun described in Example 1 on a steel base prepared by lightly grit-blasting, using the spraying conditions as described in Example 1. During the spraying silicon combines with the nickel in an exothermic reaction, greatly enhancing the thermal efficiency of the spraying and producing an excellent coating.

Example 6

Titanium is coated with nickel as described in Example 1 to produce a powder having a particle size between 100 and 325 mesh and containing 10 to 50% nickel based on the titanium-nickel total.

The nickel protects the titanium from oxidation during storage and when spraying.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the nickel and titanium combine exothermically in the flame to form a corrosion-resistant coating comprising a nickel-titanium intermetallic compound.

Example 7

Tellurium powder was coated with copper so as to form a composite having a particle size between 100 and 325 mesh and containing 50 to 80% copper based on the tellurium-copper total.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the copper and tellurium combine to form a new material.

During the spraying heat was evolved upon the combination of the copper and tellurium increasing the thermal economy of the process.

Example 8

The nickel-clad flame spray power of Example 1 is mixed with about 20% by weight of low pressure polyethylene powder and molded at a temperature of about 212° F. into the form of a rod of ⅛" diameter. The rod is sprayer, using a conventional wire-type flame spray gun sold by Metco Inc. of Westbury, N.Y., as the Metco type 4-E gun. The spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu. ft./hr. with oxygen as oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu. ft./hr.; with air as a blast gas at a pressure of 40 p.s.i. and a flow rate of 25 cu. ft./min. The end coating produced is similar to the coating produced in Example 1.

Example 9

A wire is formed by encasing a core of nickel in a tube of aluminum and drawing to a size of .125" in diameter plus or minus .002". The wire contains 82 to 84% by weight of nickel based on the aluminum-nickel total.

The wire is sprayed, using a conventional wire type flame spray gun sold by Metco Inc. of Westbury, N.Y., as the Metco type 4-E gun. Spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu. ft./hr. with oxygen as the oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu. ft./hr. Air is used as a blast gas at a pressure of 55 p.s.i. and a flow rate of 30 cu. ft./min. The end coating produced is similar to the coating produced in Example 1.

Similar results are also obtained using 55–90% by weight of nickel in the wire.

Example 10

A composite wire is formed by winding individual wires of nickel and aluminum to form a stranded wire with a diameter of .125" plus or minus .002". The wire contains 55 to 90% by weight of nickel based on the total Al–Ni. The wire is sprayed in the manner described in Example 9, with identical conditions and coating resulting.

Example 11

A silicon powder having a particle size between 140 and 325 mesh is coated with molybdenum in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The molybdenum coating and the silicon base combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

Example 12

A molybdenum powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, N.Y., under the trade name of type 2MB Plasma Flame gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using a mixture of argon and hydrogen gas as the plasma gas, with argon at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., and hydrogen at 50 p.s.i. and a flow rate of 25 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu. ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57–62 volts.

The molybdenum base and silicon coating combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

Example 13

A silicon powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The chromium coating and the silicon base combine in the heat of the flame, forming a chromium-silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

Example 14

A chromium powder having a particle size between 140 and 325 mesh is coated with silicon in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of type 2MB Plasma Flame gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu. ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57–62 volts.

The chromium base and silicon coating combine in the heat of the flame, forming a chromium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

Example 15

A zirconium powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner and a composite powder is formed containing about 45% zirconium and 60% chromium by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material in the manner described in Example 1.

The chromium coating and the zirconium base combine in the heat of the flame, forming a chromium zirconium intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures.

Example 16

A titanium powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 65% titanium and 35 to 65% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting.

The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, N.Y., under the trade name of type 2MB Plasma Flame gun. The spraying is effected at a rate of six to nine lbs of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu. ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400–500 amperes at 57–62 volts.

The titanium base and silicon coating combine exothermically in the heat of the flame, forming a titanium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

Example 17

A dysprosium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 60 to 75% dysprosium and 25 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The aluminum coating and the dysprosium base combine in the heat of the flame with a strong exothermic action, forming a dysprosium aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

Example 18

A lanthanum powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 70 to 75% lanthanum and 25 to 30% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the lanthanum base combine exothermically in the heat of the flame with a strong exothermic action, forming a lanthanum aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

Example 19

A chromium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed consisting of 60 to 62% chromium and 38 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the chromium base combine in the heat of the flame with a strong exotherimic action, forming a chromium aluminum intermetallic compound which deposits on the base as a dense, high quality coating of very high melting point and excellent oxidation-resistance.

Example 20

Example 19 is repeated except that the composite powder is formed with an aluminum core and chromium coating. Identical results are obtained.

Example 21

The nickel-clad aluminum composite powder of Example 1 is mixed with cobalt bonded tungsten carbide particle powder having a particle size range of −140 mesh +10 microns, and preferably −140 +325 mesh in proportions of:

(a) 80 weight percent tungsten carbide to 20 weight percent of the composite.

(b) 20 weight percent of the carbide to 80 weight percent of the composite, and

(c) preferably 50 weight percent each of the tungsten carbide and composite.

The powder mixtures are each flame-sprayed on a mild steel plate which has been surface-cleaned by grinding or very light sand-blast cleaning. The spraying is effected at about 8–9 inches from the plate, using a powder-type flame-spray gun as described in U.S. Patent 2,961,335, issued Nov. 22, 1960, and sold by Metco Inc. of Westbury, N.Y., under the trade name of "Thermo-Spray" powder gun. The spraying is effected at a rate of 6 to 10 lbs. per hour using acetylene gas as the fuel at a pressure of 12 p.s.i. and a flow rate of 20 to 30 cu. ft./hr. and oxygen as the oxidizing gas at a pressure of 14 p.s.i. and a flow rate of 30 to 40 cu. ft./hr.

The nickel-aluminum composite powder in the mixture reacts exothermically in the flame to provide the self-bonding properties of the mixture and, being fully molten on impact with the substrate, becomes the matrix which securely binds the tungsten carbide particles together in the coating.

Used as sprayed, or finished by proper grinding procedure, the resultant coating is of a highly wear-resistant coating material, applicable to virtually any base material and not subject to the limitations of the previously used self-fluxing alloy matrix materials which must be fused at approximately 1900° F.

Example 22

Example 21 is repeated except that in place of the grade of tungsten carbide cobalt powder grains used, cobalt-bonded tungsten carbide grains with lower cobalt content and sharp, angular shape are used.

The powder was sprayed in the manner described in Example 21. The sharp, angular edges of the initial tungsten carbide particles were retained in the coating.

The deposited coating may be suitably finished by grinding for use as a wear-resistant coating or used as deposited where the coated article is to be used as a hone or lap, the sharp edges of the carbide inclusions constituting the abrading or cutting edges.

Example 23

Example 22 is repeated except that in place of the tungsten carbide grains described, cobalt-bonded tungsten carbide particles of sharp, angular shape were used which were first coated with nickel in the manner described in Example 1, so as to produce nickel-clad particles having a size between 100 and 325 mesh and containing from 20–50% nickel based on the tungsten carbide-nickel total.

Example 24

The nickel-clad aluminum composite described in Example 1 is mixed with a columbium (niobium) powder of size between −120 mesh and +10 microns and preferably −140 +325 mesh in the proportions of 60 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and when properly finished, by grinding or other means, is a highly wear-resistant, hard coating.

Example 25

The nickel-clad aluminum composite described in Example 1 is mixed with a molybdenum powder of a size between −120 mesh and +10 microns and preferably −140 +325 mesh in the proportions of 65 weight percent molybdenum to 35 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self-bonding to

a wide variety of substrate materials and when properly finished, by grinding or other means, presents a highly wear-resistant, hard surface.

Example 26

Example 21 is repeated except in place of the tungsten carbide, other carbides such as titanium carbide, tantalum carbide, columbium carbide, chromium carbide and mixtures of the various carbides are used.

Example 27

The nickel-clad aluminum core composite from Example 21 is mixed with aluminum powder in the mesh size range −100 +325 mesh, and preferably in the −170 +325 mesh size range in the proportions of 80 weight percent nickel aluminum composite to 20 weight percent aluminum.

The mixture was sprayed in the manner described in Example 21. The coating as deposited consists of an intimate mixture of the flame-reacted nickel aluminide and aluminum securely bonded to the base and particle to particle within the coating.

Upon heat-treating in the temperature range 1250° F. to 1500° F. in reducing atmosphere, dry hydrogen for instance, the nickel aluminide and aluminum combine to form a dense, homogenous coating fused to the base material which can be used for "cathodic" protection of iron and steel subject to water and salt-water corrosion.

Example 28

The nickel-clad aluminum composite powder of Example 21 is mixed with Monel powder of a size between −100 mesh and +10 microns, and preferably between −140 and +325 mesh in the proportions 35 weight percent composite to 65 weight percent Monel.

The powder mixture was sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and the inclusion of the nickel-aluminum composite, the components of which combine exothermically in the flame to provide the self-bonding ability of the mixture, considerably increase the particle to particle bonds within the coating and decrease the permeability of the coating.

Example 29

Example 28 is repeated except that nickel and stainless steel powders are substituted for the Monel.

Example 30

Example 28 is repeated except that chromium is substituted for the Monel.

The resultant coating when properly finished, by grinding or other means, shows high resistance to abrasion, wear, and galling by other metals, and is an excellent bearing surface.

Example 31

Finely divided aluminum powder (−325 mesh) was blended with a phenolic varnish having approximately 50% solid contents so as to form a mixture having the consistency of a heavy syrup and containing 60% by weight of the metallic aluminum.

100 grams of this varnish aluminum powder mixture was added to 240 grams of nickel powder having a size between −200 and +325 mesh, and the two were thoroughly mixed, with the mixing continued until the varnish dried, leaving a fairly free-flowing powder in which all of the nickel core particles were clad with a dry film, which consisted of aluminum particles bonded to each other and to the core material by the phenolic binder. The powder is then warmed to 250° F. to insure complete drying. There were some minor agglomerates which were screened out and handmilled to reduce the same to a −100 mesh powder. The end powder consisted of approximately 15 weight percent aluminum and 85 weight percent nickel due to the loss of some aluminum during the milling. The powder is sprayed in the manner described in Example 1 producing a similar coating having, however, more than twice the tensile strength of the coating produced in Example 1.

Example 32

(a) A mixture of 6 weight percent aluminum and 94 weight percent nickel powder are thoroughly blended and pressed together in the form of cylindrical briquettes which are loaded into an aluminum tube of .375" outside diameter, after which the tube ends are welded closed. The ¾" diameter feed stock is then swaged to ⅜" diameter, then to a 3/16" diameter then to a ⅛" finished wire diameter. The wire is then annealed and coiled. The wire is then sprayed, using the conventional wire type flame spray gun sold by Metco Inc. as the Metco type 4-E gun. Spraying is effected, using acetylene at a pressure of about 15 lbs. p.s.i. and a flow rate of 37 cu. ft./hr. and oxygen as the oxidizing gas at a pressure of 38 lbs. p.s.i. and flow rate of 75 cu. ft./hr. Air is used as a blast gas at a pressure of 55 lbs. p.s.i. and flow rate of 30 cu.ft./min. The wire is sprayed at a rate of 5 ft. per minute. The spray material is deposited on a surface of ground and machine-finished, cold rolled steel with a tensile bond strength of 3820 lbs. p.s.i. The sprayed coating is hard and dense; it is wear- and oxidation-resistant and it also could serve as a base for further spraying.

(b) Example 32(a) is repeated except that chromium is used in place of the nickel powder in amounts of from 24–95 weight percent, based on the total of the aluminum and chromium. Spraying results in a high quality coating which has self-bonding properties and is resistant to oxidation at high temperatures.

(c) Example 32(a) is repeated, using columbium powder in place of the nickel powder in amounts of from 40–90 and preferably 50–55 weight percent, based on the total of the columbium and aluminum. The sprayed coating formed is a high quality coating which is resistant to oxidation at high temperatures and may be used to protect tantalum and molybdenum bases from oxidation.

(d) Example 32(a) is repeated, using tantalum powder in place of the nickel powder in amounts of 40–90 weight percent and preferably 65–75 weight percent of tantalum, based on the total of tantalum and aluminum. The sprayed coating is a dense, high quality coating which is self-bonding and is resistant to oxidation at high temperatures.

(e) Example 32(a) is repeated, using boron powder in place of the nickel powder in amounts of 40–90 weight percent, based on the total of boron and aluminum. The resulting sprayed coating is self-bonding and is resistant to oxidation at high temperatures.

(f) Example 32(e) is repeated except that the powder additionally contains 0.5 to 5 weight percent of boron, and/or 0.5 to 5 weight percent of silicon, based on the total of the components. The coating formed is similar to that obtained in Example 32(e) except that on heating to high temperature in air, a very thin, dense, adherent, protective oxide film forms on the surface of the intermetallic compound formed, which is resistant to spalling due to thermal shock, and which is believed self-healing.

(g) Example 32(a) is repeated except that tungsten carbide containing 12% binder and having a particle size below −140 mesh is added in amount of 5–70 weight percent, based on the total of the components. The resulting coating is a dense, extremely wear-resistant coating, which has self-bonding properties. This example may be further repeated, using in place of the tungsten carbide specified, crystalline tungsten carbide, aluminum oxide, diamonds or any other abrasive material.

(h) Example 32(a) is repeated. However, 1–10% by weight and preferably 1–5% by weight of titanium hydride of a size below −100 mesh and preferably below −325 mesh, based on the total of the components, is added to the core material. The results are the same as indicated

in Example 32(a) except that the coating formed is of improved physical strength, containing considerably less oxide inclusions. In place of the titanium hydride other metal hydrides may be used.

(i) Example 32(a) is repeated except that the nickel powder is replaced with a nichrome powder consisting of a chrome alloy containing 80% nickel and 20% chromium. When sprayed the wire gives a dense, self-bonding coating which is extremely oxidation-resistant.

(j) Example 32(a) is repeated except that the nickel powder is replaced with a powder mixture consisting of 80% by weight nickel and 20% by weight chrome. When sprayed the wire gives a dense, self-bonding coating which is highly oxidation-resistant.

Example 33

Table I below gives examples of further component pairs which may be used to form the powders and/or wires in accordance with the invention.

Each of the component pairs as listed in Table I below may be formed into a composite powder or wire as described above, and when flame-sprayed will exothermically react, forming an intermetallic compound and high grade coating. Thus, the component pairs may be formed into clad powders as described in Example 31 and sprayed as described therein, or formed into a composite wire as described in Example 32 and sprayed as described therein.

TABLE I

Ag Ce	As Cd	Be U	Ga Pr	Mg Sb	Si V
Al As	As Ga	Be Zr	Ga Sb	Mg Sn	Si Zr
Al Au	As In	Bi Ca	Ga Te	Na Pb	Sn Te
Al B	As Mg	Bi Ce	Ga U	Na Sb	Sn U
Al Ba	As Zn	Bi K	Ge Mg	Na Se	Sn Zr
Al Ca	B Y	Bi Li	Ge Nb	Na Sn	Te Zn
Al Ce	B Ca	Bi Mg	Ge Zr	Na Te	Mo Be
Al Co	B Cr	Bi Na	Li In	Na Tl	Nb Be
Al Cr	B Hf	Bi Se	In Te	Nb Si	Ta Be
Al La	B Nb	Bi Te	In Ru	Ni Th	V Be
Al Li	B Ta	Bi Th	K Sb	Pb Pr	Ti Be
Al Mo	B Th	Ca Pb	K Se	Pb Pu	Cr Si
Al Nb	B Ti	Ca Sn	K Sn	Pb Se	Cr Ti
Al Ni	B V	Ca Tl	K Tl	Pb Tl	Cr Zr
Al Pr	B W	Cd Li	La Pb	Pd U	Mg Te
Al Ti	B Zr	Cd Na	La Sb	Pr Sn	Ni Te
Al Zr	Ba Bi	Ce In	La Sn	Pr Tl	Si Th
Al Sb	Ba Pb	Ce Mg	La Tl	Sb Zr	Si W
Al Se	Ba Sb	Ce Pb	La Zn	Se Sn	Co Si
Al Ta	Be Co	Ce Si	Li Pb	Se Th	Mo Si
Al Te	Be Cr	Ce Sn	La Sb	Se Tl	Ni Si
Al U	Be Ni	Ce Tl	Li Sn	Cu Te	Si Ta
Al V	Be Np	Ce Zn	Li Tl	Si Ti	
Al W	Be Pu	Ga Na	Li Zn	Si U	

While the invention has been described in detail with reference to certain specific embodiments, various changes and modifications which fall within the spirit of the invention and scope of the appended claims will become apparent to the skilled artisan. The invention therefore is only intended to be limited by the appended claims or their equivalents, wherein we have endeavored to claim all inherent novelty.

We claim:

1. A flame spray material comprising a composite in a form suitable for flame spraying, formed of at least two metal components which exothermically react with each other when melted, forming an intermetallic compound and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

2. A flame spray material comprising a composite in a form suitable for flame spraying formed of at least two metal components which exothermically react with each other when melted, forming an intermetallic compound with the release of at least 3,000 gram calories per gram atom and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

3. A flame spray material comprising a composite in a form suitable for flame spraying formed of at least two metal components which exothermically react with each other when melted, forming an intermetallic compound with the release of at least 7,500 gram calories per gram atom and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

4. A flame spray material comprising a composite in a form suitable for flame spraying formed of aluminum and nickel and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

5. Composite according to claim 4 in which said aluminum is present in amount of about 10–45%, based on the total of nickel and aluminum.

6. Composite according to claim 1 in which said components are component pairs selected from the group listed in Table I above.

7. A flame spray powder in the form of individual clad particles comprising a metal nucleus and at least one coating layer of a metal differing from said nucleus and exothermically reactive therewith when melted together, forming an intermetallic compound and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

8. A flame spray powder in the form of individual clad particles comprising a metal nucleus and at least one coating layer of a metal differing from said nucleus and exothermically reactive therewith when melted together, forming an intermetallic compound, with the release of at least 3,000 gram calories per gram atom and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

9. A flame spray powder in the form of individual clad particles comprising a metal nucleus and at least one coating layer of a metal differing from said nucleus and exothermically reactive therewith when melted together, forming an intermetallic compound, with the release of at least 7,500 gram calories per gram atom and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

10. A flame spray powder according to claim 7 in which said metal nucleus and metal differing from said nucleus are component pairs selected from the group listed in Table I above.

11. A flame spray powder according to claim 7 in which said coating layer is in the form of a finely divided metal powder bound to the nucleus by a binder.

12. A flame spray powder in the form of individual clad particles comprising a nucleus of aluminum and a coating layer of nickel and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

13. Powder according to claim 12 in which said aluminum is present in amounts of about 10–45% based on the total of nickel and aluminum.

14. A flame spray powder in the form of individual clad particles comprising a nucleus of nickel and a coating layer of finely divided aluminum particles bound to the nucleus with a binder and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

15. A non-cavitating flame spray wire comprising two separate metal components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

16. A non-cavitating flame spray wire comprising two separate metal components differing from each other and capable of exothermically reacting with each other when

melted together, forming an intermetallic compound, with the release of at least 7,500 gram calories per gram atom and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

17. A non-cavitating flame spray wire comprising two separate metal components differing from each other and capable of exothermically reacting with each other when melted together, one of said components being aluminum and the other nickel and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

18. A flame spray wire comprising two separate metal components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound, with the release of 7,500 gram calories per gram atom, said components being component pairs selected from the group listed in Table I above and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

19. A flame spray wire comprising a sheath of a first metal component and a powder core of at least one second metal component, said first and second components being capable of exothermically reacting with each other when melted together, with the release of at least 7,500 gram calories per gram atom and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

20. A flame spray wire according to claim 19 in which said sheath is aluminum and said core a mixture of aluminum and nickel powder.

21. A flame spray wire comprising individual strands of two separate metal components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound, with the release of at least 7,500 gram calories per gram atom and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

22. Flame spray material according to claim 1 additionally containing a metal hydride.

23. Flame spray material according to claim 1 in which one of the said components is at least partially in the form of a hydride.

24. Flame spray material according to claim 1 additionally containing a member selected from the group consisting of boron, silicon and mixtures thereof.

25. A flame spray material comprising a composite in a form suitable for flame spraying formed of at least two metal components which exothermically react with each other when melted, said components being component pairs selected from the group consisting of Al Co, Al Cr, Al Mo, Al W, Al Ta, Al Nb, Al Ti, Al Ni, Si Nb, Si Cr, Si W, Si Co, Si Mo, Si Ni, and Si Ta and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

26. A flame spray material according to claim 25 in the form of a powder.

27. A flame spray material according to claim 25 in which one of the components is in the form of a coating on the other component.

28. A flame spray material according to claim 25 in the form of a wire.

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E 816

April 1, 1969 F. J. DITTRICH ET AL 3,436,248

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Original Filed March 25, 1965

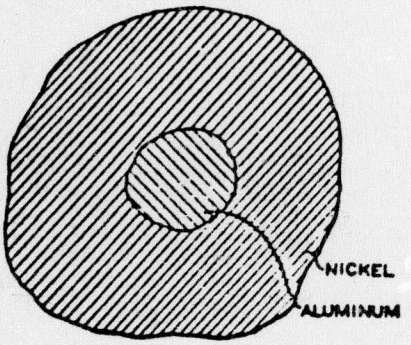

Fig. 1

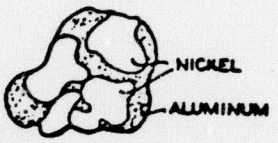

Fig. 2

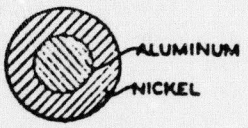

Fig. 3

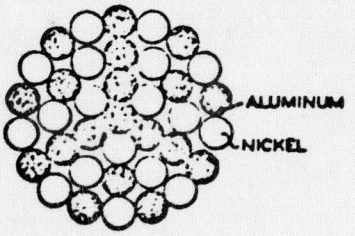

Fig. 4

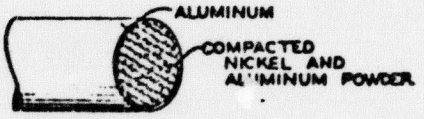

Fig. 5

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E 817

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,436,248 April 1, 1969

Ferdinand J. Dittrich et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9, line 38, "Al-Nn" should read -- Al-Ni --. Column 13, line 56, "poyder" should read -- powder --. Column 14, line 20, "end" should read -- and --. Column 15, line 32, "Ce Mg" should read -- Ge Mg --; line 33, "Ce Nb" should read -- Ge Nb --; line 34, "Ce Zr" should read -- Ge Zr --. Column 18, line 24, "Mackin et al." should read -- Mackiw et al. --.

Signed and sealed this 7th day of April 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents

E 818

United States Patent Office

3,436,248

Patented Apr. 1, 1969

3,436,248

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Ferdinand J. Dittrich, Bellmore, and Arthur P. Shepard, Flushing, N.Y., assignors to Metco, Inc., a corporation of New Jersey

Application Mar. 25, 1965, Ser. No. 442,727, now Patent No. 3,322,515, dated June 30, 1967, which is a continuation-in-part of application Ser. No. 343,705, Feb. 10, 1964. Divided and this application May 26, 1966, Ser. No. 592,238

Int. Cl. C23c 7/00, 13/02

U.S. Cl. 117—105 27 Claims

ABSTRACT OF THE DISCLOSURE

Method of coating a surface by flame spraying two or more components which will react with one another during the flame spraying to form an intermetallic compound.

This is a division of application Ser. No. 442,727, filed Mar. 25, 1965, now Patent No. 3,322,515, which was a continuation-in-part of applications, Ser. No. 72,543, filed Nov. 22, 1960, now abandoned; Ser. No. 134,544, filed Aug. 16, 1961, now Patent No. 3,254,970; Ser. No. 237,786, filed Oct. 26, 1962, now abandoned; and Ser. No. 343,705, filed Feb. 10, 1964, now abandoned.

This invention relates to the flame spraying of exothermically reacting intermetallic compound forming composites. The invention more particularly relates to the flame spraying of flame spray materials in the form of composites containing two or more components which will exothermically react with each other during the spraying, forming one or more intermetallic compounds, and to a novel group of such composites including powders and wires.

Flame spraying involves the feeding of a heat fusible material into a heating zone, wherein the same is melted or at least heat-softened, and then propelled from the heating zone in a finely divided form, generally onto a surface to be coated.

The material being sprayed is generally fed into the heating zone in the form of either a powder or a wire (the latter term designating both rods and wires). The spraying is effected in a device known as a heat-fusible material spray gun or a flame spray gun.

In the wire type flame spray gun the rod or wire of the material to be sprayed is fed into the heating zone formed by a flame of some type, where it is melted or at least heat-softened and atomized, usually by blast gas, and thence propelled in finely divided form onto the surface to be coated. The rod or wire may be a conventionally formed rod or wire of a metal, or may be formed by sintering together finely divided material, or by bonding together finely divided material by means of a plastic binder or other suitable binder which disintegrates in the heat of the heating zone, thereby releasing the material to be sprayed in finely divided form.

For spraying finely divided, i.e., powdered material, a powder type flame spray gun is used in which the powder, usually entrained in a carrier gas, is fed into the heating zone of the gun formed by a flame of some type. The powder is either melted or at least the surface of the grains heat-softened in this zone, and the thus thermally conditioned particles propelled onto a surface to provide a coating. In the powder type spray gun as no "atomizing" energy is required, a separate blast gas is often dispensed with, though the same may be supplied in order to aid in accelerating the particles and propelling them toward the surface to be coated.

The blast gas may be provided for both the wire type and powder type guns to perform the additional function of cooling the workpiece and the coating being formed thereon.

The heat for the heating zone is most commonly produced from a flame caused by the combustion of a fuel, such as acetylene, propane, natural gas, or the like, using oxygen or air as the oxidizing agent. The heat may, however, also be produced by an electrical arc flame or, in the newer type of guns, by a plasma flame. The plasma flame may in itself constitute part of an electric arc, or, in accordance with a newer development, may be in the form of a "free plasma stream," i.e., a stream of plasma which may be considered independent of the arc as it does not contribute to the electric flow between electrodes.

Heat-fusible material spray guns utilizing electric resistance heating or induction heating as the heat source have also been proposed but have not proven commercially successful except in connection with the spraying of low melting point metals, such as solders, lead and zinc.

Flame spraying in the initial stages of its commercial development was used mostly for the spraying of various metals and was often referred to as metallizing. However, the art of flame spraying extends to the spraying of a much wider group of materials, including higher melting point or refractory metals, ceramics, cermets, and the like, and such materials are of increasing commercial interest.

In the case of spraying heat-fusible materials in the initial form of a rod or wire, the rod or wire is generally of a single composition, i.e., in the form of a specific metal, alloy, ceramic, or the like. While it is true that rods or wires formed from finely divided material bound together with a binder of plastic or the like, as mentioned above, were known, the binder generally did not take part in the spraying or contribute to the coating, and merely served the purpose of maintaining the rod or wire in shape until fed into the heating zone.

In the case of flame spray powders, while powders formed of several constituents were known, the same were generally in the form of a powder mixture of the individual constituents or, at best, a particle aggregate.

One object of this invention is the spraying of the heat-fusible material in a novel form which allows the obtaining of superior results.

A further object of this invention is a novel group of flame spray materials.

These and still further objects will become apparent from the following description read in conjunction with the drawing in which:

FIG. 1 diagrammatically shows a cross-section of a grain of novel powder in accordance with the invention;

FIG. 2 is a cross-section of a further embodiment of an aggregate grain of novel flame spray powder in accordance with the invention;

FIG. 3 is a diagrammatic cross-section of an embodiment of a novel flame spray wire in accordance with the invention;

FIG. 4 shows a cross-section of a further embodiment of a novel flame spray wire in accordance with the invention; and

FIG. 5 shows a still further embodiment of a novel flame spray wire in accordance with the invention.

In accordance with the invention, the flame spraying is effected with the heat-fusible material in the form of a composite containing at least two components which will exothermically react with each other at the temperatures developed during the spraying, forming an intermetallic compound.

The term "composite" as used herein is intended to designate a structurally integral unit and does not include a mere mixture of components which may be physically

separated without any destruction of the structure. Thus, in the case of powder, the term "composite" does not include a simple mixture of individual granules of the separate components, but requires that each of the individual granules contain the separate components which will exothermically react, forming intermetallic compounds. In the case of wire, the individual components must be incorporated in a single wire. In the composite the components must be in intimate contact with each other.

In connection with powders, each grain may consist of an aggregate containing the two components which will exothermically react, forming the intermetallic compound, but preferably the individual grains of the powder are in the form of a clad composite consisting of a nucleus of one of the components and at least one coating layer of the other component. Alternatively, the composite may consist of separate, concentric coating layers of the two components and a nucleus of still a third material.

In the case of wires, the composites may be in the form of a wire having a coating sheath of one material and a core of the other, alternate coating sheaths of the components and a core of a third material, a wire formed by twisting or rolling separate wire strands of the components, a wire consisting of a sheath of one component and a core containing the other component in powder or compacted form, a wire consisting of a sheath of one component and a core containing a compacted powder mixture of this same component material and one or more other components, a wire consisting of a plastic sheath and a core containing a compacted powder mixture of components, etc.

In order for the wires to be satisfactory for spraying, the same must not cavitate at the tip when heated, and should preferably be capable of forming a pointed or slightly tapered tip when being melted and sprayed. Thus, if the wires have an outer layer or sheath of one component and an inner core of another component, the inner core cannot have a lower melting point than the outer sheath, as otherwise the inner core will initially melt, causing cavitation at the tip. For example, if the wire is composed of nickel and aluminum as the exothermically reacting components and is in the form of a core with a coating sheath, the core must be nickel and the coating sheath aluminum, as otherwise during the spraying the core will initially melt out, causing the cavitation which will interfere with a satisfactory spraying operation. The wire having the melting-point characteristics so as to allow the melting off of the tip without this cavitation, is referred to herein and in the claims as "non-cavitating wire."

As the components, any two metallics which may be melted together to form an intermetallic compound in an exothermic reaction may be used. The components should release about 3000 calories per gram atom, and preferably at least 7500 calories per gram atom in the exothermic reaction forming the intermetallic compounds. The term "calories per gram atom" as used herein denotes the number of gram calories which the average atomic weight in grams of the intermetallic compound formed will generate in so being formed. While the components are preferably present in the stoichiometric proportions required for the formation of the intermetallic compound, it is, however, possible to also have an excess of one or the other provided the relative amounts are sufficient to release the quantities of heat indicated above in the formation of the intermetallic compounds.

An extremely large number of metal components are known which can be melted together in an exothermic reaction, forming an intermetallic compound with the generation of heat. Any of these component pairs may be utilized in accordance with the invention, it only being required that the same be capable of being initially formed into the composite suitable for spraying and that the intermetallic compounds formed therefrom liberate the required amount of heat in the intermetallic compounds-formation and are suitable as components of a sprayed coating. As a general rule, components which will form intermetallic compounds having a higher melting point will liberate sufficient heat to be useful in accordance with the invention. In certain instances, however, components which will form intermetallic compounds which do not have as high a melting point, will also liberate sufficient heat in the exothermic reaction and thus be useful. Preferred components are aluminum with at least one of Co, Cr, Mo, W, Ta, Nb, Ti, or most preferably Ni; or silicon with at least one of Ti, Nb, Cr, W, Co, Mo, Ni or Ta.

While iron itself is not a satisfactory component, the same may be present in addition to another component, which in itself is satisfactory, such as in the form of an alloy therewith. This other component, however, must be present in amount sufficient to form the intermetallic compound with the other component of the composite, with the generation of sufficient heat to aid the spraying operation. Thus, for example, iron which just contains enough alloyed nickel to render the same rust-resistant, does not contain enough nickel for an effective exothermic reaction with aluminum. Generally an alloy of nickel and iron must contain at least about 12% nickel for this purpose.

FIG. 1 shows a composite powder consisting of a nucleus of aluminum and a coating layer of nickel. FIG. 2 shows an aggregate of these components; and FIGS. 3, 4 and 5 show various forms of wire containing these components, FIG. 3 showing a wire having an aluminum core with a nickel sheath, FIG. 4 showing a wire made of alternate strands of nickel and aluminum wire, as for example 18 strands of 25 gauge (.019" diameter) nickel wire marked 1, and 19 strands of 25 gauge aluminum wire marked 2; and FIG. 5 shows a sheath of aluminum filled with granules of nickel and aluminum.

Where one of the component metals is available as a metal hydride, the same may be used in this form rather than as a metal per se. When flame sprayed the hydrogen gas evolved from the hydride produces a reducing atmosphere, which in turn suppresses oxidation of the intermetallic compounds during and immediately after their formation. Thus, for example, in place of titanium, titanium hydride may be used as one of the components.

Also for the purpose of reducing oxidation a metal hydride, such as titanium hydride, may be added in a minor amount to the other components. Thus, for example, 1–10% by weight, and preferably 1–5% by weight, based on the total of the hydride and other components, may be used.

In addition, the powder granules and the wire may contain other conventional flame spray components, or be sprayed in admixture or in conjunction therewith. Thus, for example, the coated powders may additionally contain other coating layers of other flame spray components or may contain a nucleus of another flame spray material with alternate coating layers of the components which will exothermically react, forming the intermetallic. In a similar manner, the aggregates or the wires may contain further flame spray components, and in the case of powders, the same may additionally be admixed with any other desired flame spray powder.

The clad powders, in accordance with the invention, may be formed in any known or desired manner, and preferably by the known chemical plating processes, in which coating material is deposited on a seed or nucleus of another material, or in which multiple layers of various materials are built up on the seed material, or in which various materials are co-deposited in a single layer on the seed material.

A mode of forming the clad powders involves the depositing of a metal from a solution by reduction on a seed or nucleus, such as by the hydrogen reduction of ammoniacal solutions of nickel and ammonium sulfate on a seed powder catalyzed by the addition of anthraquinone. It is also possible to form the coating by the use of other known coating processes, such as coating by vapor de-

position, by the thermal decomposition of metal carbonyls, by hydrogen reduction of metal halide vapors, by thermal deposition of halides, hydrides, carbonyls, organo metals, or other volatile compounds, or by displacement gas plating and the like.

A preferred and greatly simplified mode of forming the clad powders in accordance with the invention is the depositing of one component as a coating in the form of a paint on the other component. Thus, one of the components which is to form the coating or cladding, may be dispersed in finely divided form in a binder or lacquer so as, in effect, to form a paint in which "is component corresponds to the pigment. The paint is then used to coat core particles of the other component and the binder or lacquer allowed to set or dry. The binder material is preferably a resin which does not depend on solvent evaporation in order to form a dried or set film, and which film will decompose or break down in the heat of the spraying process. The binder, for example, may be a phenolic varnish or any other known or conventional varnish, preferably containing a resin as the varnish solids. The component which is initially mixed with the binder or varnish should preferably be as finely divided as possible, as for example −325 mesh. The other component which constitutes the core should be approximately or only slightly below the particle size ultimately desired for the spray powder. The coating of the core component with the "paint" may be effected in any known or desired manner, and it is simply necessary to mix the two materials together and allow the binder to dry or set, which will result in a fairly free-flowing powder consisting of the core component coated with a cladding of the other component bound in the binder.

The aggregates may be formed by compacting or briquetting the various components into the individual granules, or into larger aggregates and then breaking these aggregates into the granules.

The wires may be formed in the known conventional manner for forming wires with various components as, for example, by shrinking a sheath on a core, by forming the core with powder, by twisting the component wires, followed by rolling, drawing, swaging, or the like if desired.

In accordance with one mode of manufacture, one of the components may be formed into a tube or sheath and filled with a powder of the other component or a powder comprising a mixture of the two components, or containing additional components. The tube ends are then sealed and the wire reduced to the desired wire diameter by swaging, rolling or drawing. Preferably the powder or powder mixture is first compressed into cylindrical briquettes before being placed in the sheath or core. The sealing of the tube ends after loading with the powder or powder mixture can be effected, for instance, by insertion of a plug, for example of the metal of the sheath, by welding, twisting, crimping, or the like.

Powders in accordance with the invention should have the general over-all shape and size of conventional, flame-spray powders, and thus for example should have a size between −60 mesh and +3 microns and preferably −140 mesh and +10 microns (U.S. Standard screen mesh size). Most preferably the powder should be as uniform as possible in grain size, with the individual grains not varying by more than 250 microns and preferably 75 microns.

Depending on the particular flame spray process and the desired purpose, the composite powders may be sprayed per se or in combination with other different composite powders, or in combination with other conventional flame spray powders or powder components.

While the powders are preferably sprayed, as such, in a powder-type of flame spray gun, it is also possible to combine the same in the form of a wire or rod, using a plastic or similar binder, which decomposes in the heating zone of the gun, or in certain cases the powders may be compacted and/or sintered together in the form of a rod or wire. The wires must have the conventional sizes and accuracy tolerances for flame spray wires, and thus for example may vary in size between ¼" and 20 gauge, and are preferably of the following sizes: 3/16" +.0005", −.0025", ⅛" +.0005", −.0025", 11 gauge +.0005", −.0025", and 15 gauge +.001", with a smooth, clean finish free from surface marks, blemishes, or defects. The wires are sprayed in the conventional manner, using conventional wire-type flame spray guns.

In combining, in the exothermic reaction, forming the intermetallic compound, the components generate heat in situ in the actual material which is to form at least a part of the coating. This is to be distinguished from flame-spray processes and materials in which heat is generated by a reaction, such as an oxidation reaction, in which a foreign and non-metallic element is introduced and in which undesirable components may be produced. Aside from greatly contributing to the thermal efficiency of the process, the heat generated in situ in the formation of the intermetallic compound produces novel results, in many instances forming a denser, more adhering coating, having characteristics of at least a partially fused coating. In many instances the coating has self-bonding characteristics, so that special surface preparation, other than a good cleaning, is not required. The spraying in all other respects is effected in the conventional, well-known manner, using conventional flame spray equipment, and the conventional surface preparation may be utilized, if desired. The composites in accordance with the invention may be sprayed in conjunction with, or in addition to, other flame spray materials conventionally used in the art, or may be sprayed in combination or conjunction with the others.

The use of the composites as, for example, the nickel-aluminum composites, will generally improve the bond of the total sprayed material, and thus of the other component or components to the substrate, sometimes making the mixture self-bonding. The particle bond will be improved and the coating will be denser, so that its porosity may be decreased. In general, as little as 10% by weight of the composites in accordance with the invention will be sufficient to substantially improve the bonding characteristics and decrease the porosity of other flame spray materials, such as conventional flame spray metals, alloys or ceramics. There is, of course, no upper limit on the amount, as the composite may be sprayed per se, but generally at least about 20% by weight of the other component is required if this component is to have a pronounced effect on the characteristics of the coating.

The following examples are given by way of illustration and not limitation:

Example 1

(a) An aluminum powder having a particle size between −140 mesh and +325 mesh (U.S. Standard screen size) is coated with nickel in the known manner by the hydrogen reduction of an ammoniacal solution of nickel and ammonium sulphate, using anthraquinone as the coating catalyst. The reduction is effected at a temperature between about 300 and 350° F. in a mechanically agitated autoclave using solutions containing 40–50 grams per liter of nickel and 10–400 grams per liter of $(NH_4)_2SO_4$ and 20–30 grams per liter of NH_3. About .2 gram per liter of anthraquinone is used as the catalyst and the autoclave is pressurized with hydrogen at a pressure of about 300 lbs. p.s.i.g. After the nickel solution is depleted and the aluminum coated with an initial coating of nickel, the solution is discharged from the autoclave and replenished with a fresh solution which need not contain further amounts of the anthraquinone coating catalyst, as the initially formed nickel coating in itself acts as a catalyst. The cycle is continuously repeated until a composite powder is formed containing about 16 to 18% by weight aluminum and 84 to 82% by weight of nickel, and a size of −100 to +270 mesh.

The powder thus formed is flame-sprayed on a mild steel plate which has been surface-cleaned with emery cloth. The spraying is effected at about 9 inches from the plate, using a powder type flame-spray gun as described in U.S. Patent 2,961,335, issued Nov. 22, 1960 and sold by Metco Inc. of Westbury, Long Island, under the trade name of "Thermospray" powder gun. The spraying is effected at a rate of 6 to 9 lbs. of powder per hour, using acetylene gas as the fuel at a pressure of 10 p.s.i. and a flow rate of 17 to 25 cu. ft./hr. and oxygen as the oxidizing gas at a pressure of 12 p.s.i. and a flow rate of 29 to 35 cu. ft./hr.

The nickel coating and the aluminum base combine in the heat of the flame with a strong exothermic action, forming a mixture of nickel aluminum-intermetallic compounds which deposit on the base as a dense, high quality coating which exhibits self-bonding characteristics. A coating layer of .002"–.004" thickness is built up in this manner. The coating may be used as a base material for spraying of further layers of different metals or the like, and serves as an excellent intermediate bonding layer.

The coating layer may also be built up to a greater thickness as, for example, .010"–.020", for use as an oxygen barrier undercoat, or to even greater thickness as, for example, .020"–.040" or thicker as a wear-resistant-oxidation-resistant surface.

Due to its self-bonding characteristics the sprayed coating will adhere to a base without the conventional surface preparation or roughening, and due to the natural characteristics of a sprayed material, will allow further materials to be sprayed thereon with good bonding. The coating formed from the powder has excellent oxidation-resistant characteristics even at high temperatures and in oxidizing atmospheres, and will for example prevent the oxidation of base materials, such as molybdenum or the like. The sprayed coatings may be used as a lining in metal-melting crucibles or molten metal-handling equipment, and will not be wetted or penetrated by many molten metals, including self-fluxing alloys. Coatings formed of the sprayed material also show good potential as high temperature, wear-resistant coatings.

When the example is repeated on a molybdenum rod of 3/16" diameter, with a coating between .010"–.012" thick, the coated rod may be repeatedly heated to approximately 2000° F. in air, in an electric furnace and cooled to room temperature with no visible oxidation occurring.

Similar results may also be obtained if the composite powder contains 10–45% by weight of aluminum and 55–90% by weight of nickel.

(b) Example 1(a) is repeated, using, however, cobalt in place of the nickel. Comparable results are obtained.

(c) Example 1(a) is repeated, using titanium hydride (TiH_2) powder in place of the aluminum and in an amount of 25–85 weight percent, and preferably 60–85 weight percent of the total. The coating formed upon spraying is hard and dense, and when sprayed on a smooth, pressed and sintered Al_2O_3 substrate, an excellent bond is formed. The spraying may be effected with an oxygen-hydrogen or oxygen-acetylene flame.

Example 2

Example 1 is repeated with the spraying being effected in turn on the following bases and prepared in the following manner:

Low alloy steels and stainless steels, smooth-ground to remove surface contamination; copper and copper base alloys, rough-ground or light-grit-blasted; aluminum and aluminum base alloys, rough-ground or light-grit-blasted; magnesium, rough-ground or light-grit-blasted; and titanium, rough-ground or light-grit-blasted.

In each case when a further material, such as steel, alumina or the like, was sprayed over the coating in the conventional and well-known manner, the same was bonded with a tenacious bond, though if this material had been initially sprayed on the surface as prepared in the manner indicated above, a satisfactory bond would not be obtained.

Example 3

The nickel-clad powder of Example 1 is mixed with an Al_2O_3 powder having a particle size between 62 microns and 10 microns, in the ratio of about 40% of the nickel-clad powder with 60% by weight of the ceramic. The powder is sprayed, using the gun described in Example 1, on a mild steel plate which has been surface-cleaned by smooth grinding. Spraying is effected at a distance of about 9" from the plate at a rate of about 4 to 8 lbs. of powder per hr., using acetylene at a pressure of 10 lbs. p.s.i. and a flow rate of 17–25 cu. ft./hr., and oxygen at a pressure of 12 p.s.i. and a flow rate of 29–35 cu. ft./hr.

A self-bonding cermet coating is formed which showed excellent thermal shock-resistance, hardness, abrasion-resistance, and which strongly inhibited oxidation of the base.

It is possible to vary the percentages of the ceramic in the mixture between 5 and 85% in order to vary the properties of the coating. With an increased amount of the intermetallic compound in the cermet coating formed, the bonding and thermal shock-resistant properties increased, whereas with an increased amount of the ceramic, the hardness and wear-resistant properties of the coating are increased and the thermal conductivity decreased.

Example 4

Example 3 is repeated, using the following materials in place of the aluminum oxide:

Zirconia, calcium zirconate, magnesium zirconate, spinel, ceric oxide, hafnium oxide, rare earth oxides, molybdenum disilicide, tungsten silicide, chromium silicide, titanium silicide, tungsten carbide, titanium carbide and chromium carbide.

In each case an excellent coating was formed.

Example 5

A nucleus of silicon powder is coated with nickel to form a nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 75–85% nickel based on the silicon-nickel total. The composite powder is sprayed with the flame spray gun described in Example 1 on a steel base prepared by lightly grit-blasting, using the spraying conditions as described in Example 1. During the spraying silicon combines with the nickel in an exothermic reaction, greatly enhancing the thermal efficiency of the spraying and producing an excellent coating.

Example 6

Titanium is coated with nickel as described in Example 1 to produce a powder having a particle size between 100 and 325 mesh and containing 10 to 50% nickel based on the titanium-nickel total.

The nickel protects the titanium from oxidation during storage and when spraying.

Upon spraying in the manner described in Example 1, on a base material prepared by grit blasting, the nickel and titanium combine exothermically in the flame to form a corrosion-resistant coating comprising a nickel-titanium intermetallic compound.

Example 7

Tellurium powder was coated with copper so as to form a composite having a particle size between 100 and 325 mesh and containing 50 to 80% copper based on the tellurium-copper total.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the copper and tellurium combine to form a new material.

During the spraying heat was evolved upon the combination of the copper and tellurium, increasing the thermal economy of the process.

Example 8

The nickel-clad flame spray powder of Example 1 is mixed with about 20% by weight of low pressure polyethylene powder and molded at a temperature of about 212° F. into the form of a rod of ⅛" diameter. The rod is sprayed, using a conventional wire-type flame spray gun sold by Metco Inc. of Westbury, Long Island, as the Metco-type 4-E gun. The spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu. ft./hr. with oxygen as oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu. ft./hr.; with air as a blast gas at a pressure of 40 p.s.i. and a flow rate of 25 cu. ft./min. The end coating produced is similar to the coating produced in Example 1.

Example 9

A wire is formed by encasing a core of nickel in a tube of aluminum and drawing to a size of .125" in diameter plus or minus .002". The wire contains 82 to 84% by weight of nickel based on the aluminum-nickel total.

The wire is sprayed, using a conventional wire type flame spray gun sold by Metco Inc. of Westbury, Long Island, as the Metco-type 4-E gun. Spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu. ft./hr. with oxygen as the oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu. ft./hr. Air is used as a blast gas at a pressure of 55 p.s.i. and a flow rate of 30 cu. ft./min. The end coating produced is similar to the coating produced in Example 1.

Similar results are also obtained using 55–90% by weight of nickel in the wire.

Example 10

A composite wire is formed by winding individual wires of nickel and aluminum to form a stranded wire with a diameter of .125" plus or minus .002". The wire contains 55 to 90% by weight of nickel based on the total Al–Ni. The wire is sprayed in the manner described in Example 9, with identical conditions and coating resulting.

Example 11

A silicon powder having a particle size between 140 and 325 mesh is coated with molybdenum in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The molybdenum coating and the silicon base combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

Example 12

A molybdenum powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of type 2MB plasma flame gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using a mixture of argon and hydrogen gas as the plasma gas, with argon at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., and hydrogen at 50 p.s.i. and a flow rate of 25 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu. ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400–500 amperes at 57–62 volts.

The molybdenum base and silicon coating combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

Example 13

A silicon powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The chromium coating and the silicon base combine in the heat of the flame, forming a chromium-silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

Example 14

A chromium powder having a particle size between 140 and 325 mesh is coated with silicon in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the tradename of Type 2MB plasma flame gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu.ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400–500 amperes at 57–62 volts.

The chromium base and silicon coating combine in the heat of the flame, forming a chromium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

Example 15

A zirconium powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner and a composite powder is formed containing about 45% zirconium and 60% chromium by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material in the manner described in Example 1.

The chromium coating and the zirconium base combine in the heat of the flame, forming a chromium zirconium intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures.

Example 16

A titanium powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 65% titanium and 35 to 65% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the

plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type 2MB plasma flame gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu. ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57-62 volts.

The titanium base and silicon coating combine exothermically in the heat of the flame, forming a titanium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

Example 17

A dysporsium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 60 to 75% dysprosium and 25 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The aluminum coating and the dysprosium base combine in the heat of the flame with a strong exothermic action, forming a dysprosium aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

Example 18

A lanthanum powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 70 to 75% lanthanum and 25 to 30% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the lanthanum base combine exothermically in the heat of the flame with a strong exothermic action, forming a lanthanum aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

Example 19

A chromium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed consisting of 60 to 62% chromium and 38 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the chromium base combine in the heat of the flame with a strong exothermic action, forming a chromium aluminum intermetallic compound which deposits on the base as a dense, high quality coating of very high melting point and excellent oxidation-resistance.

Example 20

Example 19 is repeated except that the composite powder is formed with an aluminum core and chromium coating. Identical results are obtained.

Example 21

The nickel-clad aluminum composite powder of Example 1 is mixed with cobalt bonded tungsten carbide particle powder having a particle size range of −140 mesh +10 microns, and preferably −140 +325 mesh in proportions of:

(a) 80 weight percent tungsten carbide to 20 weight percent of the composite.

(b) 20 weight percent of the carbide to 80 weight percent of the composite, and

(c) preferably 50 weight percent each of the tungsten carbide and composite.

The powder mixtures are each flame-sprayed on a mild steel plate which has been surface-cleaned by grinding or very light sand-blast cleaning. The spraying is effected at about 8-9 inches from the plate, using a powder-type flame-spray gun as described in U.S. Patent 2,961,335 issued Nov. 22, 1960, and sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of "Thermo-Spray" powder gun. The spraying is effected at a rate of 6 to 10 lbs. per hour using acetylene gas as the fuel at a pressure of 12 p.s.i. and a flow rate of 20 to 30 cu. ft./hr. and oxygen as the oxidizing gas at a pressure of 14 p.s.i. and a flow rate of 30 to 40 cu. ft. hr.

The nickle-aluminum composite powder in the mixture reacts exothermically in the flame to provide the self-bonding properties of the mixture and, being fully molten on impact with the substrate, becomes the matrix which securely binds the tungsten carbide particles together in the coating.

Used as sprayed, or finished by proper grinding procedure, the resultant coating is of a highly wear-resistant coating material, applicable to virtually any base material and not subject to the limitations of the previously used self-fluxing alloy matrix materials which must be fused at approximately 1900° F.

Example 22

Example 21 is repeated except that in place of the grade of tungsten carbide cobalt powder grains used, cobalt-bonded tungsten carbide grains with lower cobalt content and sharp, angular shape are used.

The powder was sprayed in the manner described in Example 21. The sharp, angular edges of the initial tungsten carbide particles were retained in the coating.

The deposited coating may be suitably finished by grinding for use as a wear-resistant coating or used as deposited where the coated article is to be used as a hone or lap, the sharp edges of the carbide inclusions constituting the abrading or cutting edges.

Example 23

Example 22 is repeated except that in place of the tungsten carbide grains described, cobalt-bonded tungsten carbide particles of sharp, angular shape were used which were first coated with nickel in the manner described in Example 1, so as to produce nickel-clad particles having a size between 100 and 325 mesh and containing from 20–50% nickel based on the tungsten carbide-nickel total.

Example 24

The nickel-clad aluminum composite described in Example 1 is mixed with a columbium (niobium) powder of size between −120 mesh and +10 microns and preferably −140 +325 mesh in the proportions of 60 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and when properly finished, by grinding or other means, is a highly wear-resistant, hard coating.

Example 25

The nickel-clad aluminum composite described in Example 1 is mixed with a molybdenum powder of a size between −120 mesh and +10 microns and preferably −140 +325 mesh in the proportions of 65 weight percent molybdenum to 35 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and when properly

finished, by grinding or other means, presents a highly wear-resistant, hard surface.

Example 26

Example 21 is repeated except in place of the tungsten carbide, other carbides such as titanium carbide, tantalum carbide, columbium carbide, chromium carbide and mixtures of the various carbides are used.

Example 27

The nickel-clad aluminum core composite from Example 21 is mixed with aluminum powder in the mesh size range −100 +325 mesh, and preferably in the −170 +325 mesh size range in the proportions of 80 weight percent nickel aluminum composite to 20 weight percent aluminum.

The mixture was sprayed in the manner described in Example 21. The coating as deposited consists of an intimate mixture of the flame-reacted nickel aluminide and aluminum securely bonded to the base and particle to particle within the coating.

Upon heat-treating in the temperature range 1250° F. to 1500° F. in reducing atmosphere, dry hydrogen for instance, the nickel aluminide and aluminum combine to form a dense, homogenous coating fused to the base material which can be used for "cathodic" protection of iron and steel subject to water and salt-water corrosion.

Example 28

The nickel-clad aluminum composite powder of Example 21 is mixed with Monel powder of a size between −100 mesh and +10 microns, and preferably between −140 and +325 mesh in the proportions 35 weight percent composite to 65 weight percent Monel.

The powder mixture was sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and the inclusion of the nickel-aluminum composite, the components of which combine exothermically in the flame to provide the self-bonding ability of the mixture, considerably increase the particle to particle bonds within the coating and decrease the permeability of the coating.

Example 29

Example 28 is repeated except that nickel and stainless steel powders are substituted for the Monel.

Example 30

Example 28 is repeated except that chromium is substituted for the Monel.

The resultant coating when properly finished, by grinding or other means, shows high resistance to abrasion, wear, and galling by other metals, and is an excellent bearing surface.

Example 31

Finely divided aluminum poyder (−325 mesh) was blended with a phenolic varnish having approximately 50% solid contents so as to form a mixture having the consistency of a heavy syrup and containing 60% by weight of the metallic aluminum.

100 grams of this varnish aluminum powder mixture was added to 240 grams of nickel powder having a size between −200 and +325 mesh, and the two were thoroughly mixed, with the mixing continued until the varnish dried, leaving a fairly free-flowing powder in which all of the nickel core particles were clad with a dry film, which consisted of aluminum particles bonded to each other and to the core material by the phenolic binder. The powder is then warmed to 250° F. to insure complete drying. There were some minor agglomerates which were screened out and hand-milled to reduce the same to a −100 mesh powder. The end powder consisted of approximately 15 weight percent aluminum and 85 weight percent nickel due to the loss of some aluminum during the milling. The powder is sprayed in the manner described in Example 1 producing a similar coating having, however, more than twice the tensile strength of the coating produced in Example 1.

Example 32

(a) A mixture of 6 weight percent aluminum and 94 weight percent nickel powder are thoroughly blended and pressed together in the form of cylindrical briquettes which are loaded into an aluminum tube of .375" outside diameter, after which the tube ends are welded closed. The ¾" diameter feed stock is then swaged to ¼" diameter, then to a 7/16" diameter and then to a 1/8" finished wire diameter. The wire is then annealed and coiled. The wire is then sprayed, using the conventional wire type flame spray gun sold by Metco Inc. as the Metco Type 4-E gun. Spraying is effected, using acetylene at a pressure of about 15 lbs. p.s.i. and a flow rate of 37 cu. ft./hr. and oxygen as the oxidizing gas at a pressure of 38 lbs. p.s.i. and flow rate of 75 cu. ft./hr. Air is used as a blast gas at a pressure of 55 lbs. p.s.i. and flow rate of 30 cu. ft./min. The wire is sprayed at a rate of 5 ft. per minute. The spray material is deposited on a surface of ground and machine-finished, cold rolled steel with a tensile bond strength of 3820 lbs. p.s.i. The sprayed coating is hard and dense; it is wear- and oxidation-resistant and it also could serve as a base for further spraying.

(b) Example 32(a) is repeated except that chromium is used in place of the nickel powder in amounts of from 24–95 weight percent, based on the total of the aluminum and chromium. Spraying results in a high quality coating which has self-bonding properties and is resistant to oxidation at high temperatures.

(c) Example 32(a) is repeated, using columbium powder in place of the nickel powder in amounts of from 40–90 and preferably 50–55 weight percent, based on the total of the columbium and aluminum. The sprayed coating formed is a high quality coating which is resistant to oxidation at high temperatures and may be used to protect tantalum and molybdenum bases from oxidation.

(d) Example 32(a) is repeated, using tantalum powder in place of the nickel powder in amounts of 40–90 weight percent and preferably 65–75 weight percent of tantalum, based on the total of tantalum and aluminum. The sprayed coating is a dense, high quality coating which is self-bonding and is resistant to oxidation at high temperatures.

(e) Example 32(a) is repeated, using boron powder in place of the nickel powder in amounts of 40–90 weight percent, based on the total of boron and aluminum. The resulting sprayed coating is self-bonding and is resistant to oxidation at high temperatures.

(f) Example 32(c) is repeated except that the powder additionally contains 0.5 to 5 weight percent of boron, and/or 0.5 to 5 weight percent of silicon, based on the total of the components. The coating formed is similar to that obtained in Example 32(c) except that on heating to high temperature in air, a very thin, dense, adherent, protective oxide film forms on the surface of the intermetallic compound formed, which is resistant to spalling due to thermal shock, and which is believed self-healing.

(g) Example 32(a) is repeated except that tungsten carbide containing 12% binder and having a particle size below −140 mesh is added in amount of 5–70 weight percent, based on the total of the components. The resulting coating is a dense, extremely wear-resistant coating, which has self-bounding properties. This example may be further repeated, using in place of the tungsten carbide specified, crystalline tungsten carbide, aluminum oxide, diamonds or any other abrasive material.

(h) Example 32(a) is repeated. However, 1–10% by weight and preferably 1–5% by weight of titanium hydride of a size below −100 mesh and preferably below −325 mesh, based on the total of the components, is added to the core material. The results are the same as indicated in Example 32(a) except that the coating formed is of im-

proved physical strength, containing considerably less oxide inclusions. In place of the titanium hydride other metal hydrides may be used.

(i) Example 32(a) is repeated except that the nickel powder is replaced with a nichrome powder consisting of a chrome alloy containing 80% nickel and 20% chromium. When sprayed the wire gives a dense, self-bounding coating which is extremely oxidation-resistant.

(j) Example 32(a) is repeated except that the nickel powder is replaced with a powder mixture consisting of 80% by weight nickel and 20% by weight chrome. When sprayed the wire gives a dense, self-bounding coating which is highly oxidation resistant.

Example 33

Table I below gives examples of further component pairs which may be used to form the powders and/or wires in accordance with the invention.

Each of the component pairs as listed in Table I below may be formed into a composite powder or wire as described above, and when flame-sprayed will exothermically react, forming an intermetallic compound and high grade coating. Thus, the component pairs may be formed into clad powders as described in Example 31 and sprayed as described therein, or formed into a composite wire as described in Example 32 and sprayed as described therein.

TABLE 1

Ag Ce	Ga Pr
Al As	Ga Sb
Al Au	Ga Te
Al B	Ga U
Al Ba	Ce Mg
Al Ca	Ce Nb
Al Ce	Ce Zr
Al Co	H V
Al Cr	Li In
Al La	In Te
Al Li	In Ru
Al Mo	K Sb
Al Nb	K Se
Al Ni	K Sn
Al Pr	K Te
Al Ti	La Pb
Al Zr	La Sb
Al Sb	La Sn
Al Se	La Te
Al Ta	La Zn
Al Te	Li Pb
Al U	Li Sb
Al V	Li Sn
Al W	Li Tl
As Cd	Li Zn
As Ga	Mg Sb
As In	Mg Sn
As Mg	Na Pb
As Zn	Na Sb
B Y	Na Se
B Co	Na Sn
B Cr	Na Te
B Hf	Na Tl
B Nb	Nb Si
B Ta	Ni Th
B Th	Pb Pr
B Ti	Pb Pu
B V	Pb Se
B W	Pb Tl
B Zr	Pd U
Ba Bi	Pr Sn
Ba Pb	Pr Tl
Ba Sb	Sb Zr
Be Co	Se Sn
Be Cr	Se Th
Be Ni	Se Tl
Be Nb	Cu Te
Be Pu	Si Ti
Be U	Si U

TABLE 1 Continued

Be Zr	Si V
Bi Ca	Si Zr
Bi Ce	Sn Te
Bi K	Sn U
Bi Li	Sn Zr
Bi Mg	Te Zn
Bi Na	Mo Be
Bi Se	Nb Be
Bi Te	Ta Be
Bi Th	V Be
Ca Pb	Ti Be
Ca Sn	Cr Si
Ca Tl	Cr Ti
Cd Li	Cr Zr
Cd Na	Mg Te
Ce In	Ni Te
Ce Mg	Si Th
Ce Pb	Si W
Ce Si	Co Si
Ce Sn	Mo Si
Ce Tl	Ni Si
Ce Zn	Si Ta
Ga Na	

We claim:

1. In the flame spray process in which a heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in such condition out of said zone in finely divided form onto a substrate, the improvement which comprises passing the heat-fusible material into said zone in the form of a composite comprising at least two distinct, components unalloyed together as a single alloy and in proportion and form sufficient to exothermically react with each other at the temperature developed in the heating zone, forming an intermetallic compound.

2. Improvement according to claim 1 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.

3. Improvement according to claim 1 in which said components are components which exothermically react with each other, with the release of at least 7,500 gram calories per gram atom.

4. Improvement according to claim 1 in which one of said components is aluminum and the other nickel.

5. Improvement according to claim 4, in which said aluminum is present in amount of about 10 to 45% by weight, based on the total of nickel and aluminum.

6. Improvement according to claim 1 in which said components are component pairs selected from the group listed in Table I above.

7. Improvement according to claim 1 in which said composite contains at least one additional flame spray material.

8. Improvement according to claim 1 in which said composite is sprayed in conjunction with at least one further flame spray material.

9. In the flame spray process in which heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form onto a substrate, the improvement which comprises passing the heat-fusible material into said zones in the form of individual clad powder particles comprising a nucleus and a coating layer which will exothermically react with the nucleus at the temperature developed in the heating zone, forming an intermetallic compound.

10. Improvement according to claim 9 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.

11. Improvement according to claim 9 in which said components are components which exothermically react

with each other, with the release of at least 7,500 gram calories per gram atom.

12. Improvement according to claim 9 in which said nucleus is aluminum and said coating layer nickel.

13. Improvement according to claim 12 in which said aluminum is present in amount of about 10–45%, based on the total of nickel and aluminum.

14. Improvement according to claim 9 in which the nucleus and coating layers are selected from the members of the group consisting of the pairs listed in Table I.

15. Improvement according to claim 9 in which said coating layer consists of fine particles bound to said nucleus by a binder.

16. Improvement according to claim 9 in which said clad powder particles are in admixture with another flame spray powder.

17. In the flame spray process in which heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form onto a substrate, the improvement which comprises passing the heat-fusible material into said zone in the form of a composite, non-cavitating wire comprising at least two components which exothermically react with each other at the temperatures developed in the heating zone, forming an intermetallic compound.

18. Improvement according to claim 17 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.

19. Improvement according to claim 17 in which said components are components which exothermically react with each other, with the release of at least 7,500 gram calories per gram atom.

20. Improvement according to claim 17 in which one of said components is aluminum and the other nickel.

21. Improvement according to claim 20 in which said aluminum is present in amount of about 10–45% by weight, based on the total of nickel and aluminum.

22. Improvement according to claim 17 in which said components are component pairs selected from the group listed in Table I above.

23. Improvement according to claim 17 in which said wire is in the form of a sheath of one component containing a powder of the other component, said sheath being of a component having a lower melting point than the other component.

24. Improvement according to claim 23 in which said sheath is an aluminum sheath and in which said core is a compacted mixture of aluminum and nickel powder.

25. Improvement according to claim 17 in which said wire is a multi-strand wire with individual strands of said components.

26. Improvement according to claim 1 in which the heat-fusible material additionally contains a metal hydride.

27. Process according to claim 47 in which one of said components is at least partially in the form of a hydride.

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U.S. Cl. X.R.

117—105.2

E 827

Feb. 11, 1941. P. A. BLEAKLEY 2,231,247

METHOD OF FORMING COMPOSITE METAL STRUCTURES

Filed Feb. 12, 1938

Fig. 1.

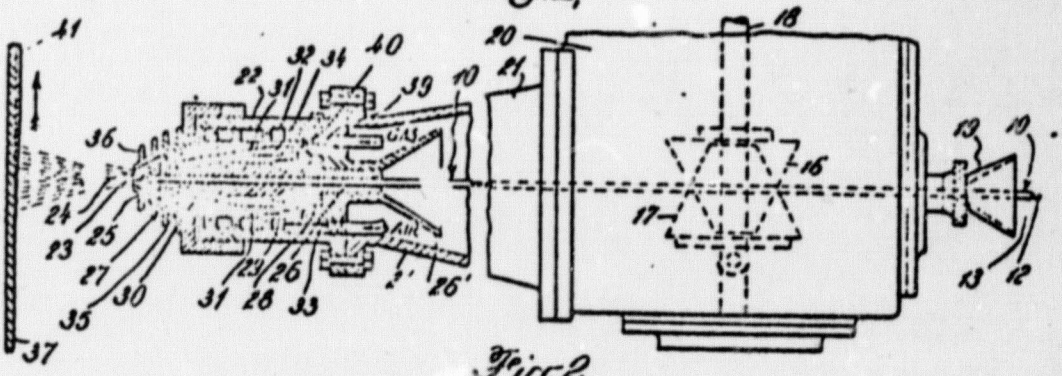


Fig. 2.

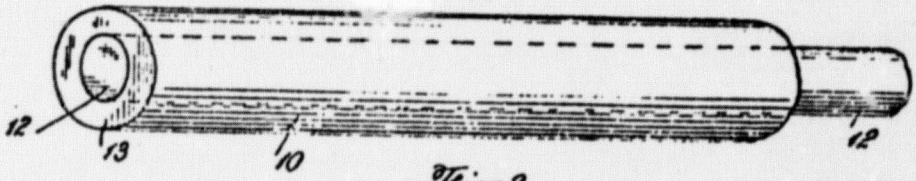
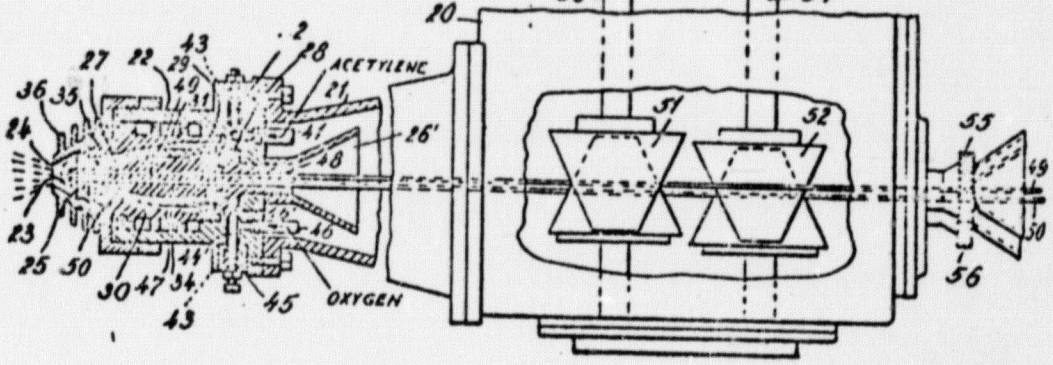


Fig. 3.

Fig. 4.



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Patented Feb. 11, 1941 E 828 2,231,247

UNITED STATES PATENT OFFICE

2,231,247

METHOD OF FORMING COMPOSITE METAL STRUCTURES

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Application February 12, 1936, Serial No. 63,588

2 Claims. (Cl. 91—70.2)

This invention relates to a method of forming composite structures, and has particular reference to method for spraying mixed molten metals or other materials, or mixtures of molten metals and non-metals, and the like, to form structures for various uses.

In copending application Serial No. 63,587 filed February 12, 1936, there are described a composite metal structure, and the present invention is directed to the method of making the said composite metal structure.

An example of a composite metal structure, which is effectively made in a superior form with the apparatus of this invention, is a copper-lead bearing liner, which has been made heretofore with indifferent and non-uniform results by means of centrifugal casting apparatus or by means of a furnace by the simultaneous quiescent fusion method. The principal reason that intimate mixtures of finely-divided copper and lead have not been readily secured in proper proportions heretofore is because the lead vaporizes at the melting point of copper and with the former apparatus and methods it cannot be enmeshed in a copper matrix with any suitable degree of distribution and only in small volume before escaping.

In accordance with the present invention, method is provided for simultaneously melting two or more materials under pressure in a substantially closed melting chamber at a temperature greatly in excess of their normal melting points, and then simultaneously conveying them in this mixed, molten condition to the surface of application in the form of a finely-divided spray, by means of and within a high pressure tubular envelope of a gas, which sufficiently maintains the mixed materials in their molten or plastic state, and which also protects the molten metal against oxidation by means of an included neutralizing agent in the gas of the envelope, or, by means of an active agent in the gas of the envelope, converts, reduces, or reacts with one or more of the metals to change its physical or chemical structure.

The preferred apparatus for practicing the method of this invention includes a mechanism for continuously and simultaneously feeding two or more metals or other materials for melting to supermolten condition under high pressure within a substantially closed melting chamber by means of an oxy-acetylene, oxy-butane or other high combustible gas flame in the presence of combustion-supporting gas, and being provided with means for supplying the aforementioned envelope gas at high pressure over the inner surface of the melting chamber and out of a restricted orifice therein, to carry the molten metals or materials at high pressure and velocity in a finely-divided state within its core to the surface of application. The pressure at which the metals or materials are maintained during their molten condition precludes vaporization of the lower melting metals or materials, and their high velocity of travel reduces the time that they remain in the highly heated state and thus aids in retarding vaporization of such low melting metals or materials.

The plurality of metals or other materials, or metals and nonmetals, to be combined in the ultimate composite structure, are preferably provided in the form of strands, which are separately but simultaneously fed to the melting chamber at a rate determined by the degree of mixture desired of the plurality of materials in the finished structure, or in the form of a built-up rod or wire of the plurality of materials, each element of which has a cross-sectional area determined by the proportion of the materials desired in the finished structure, this rod or wire being fed into the melting chamber as a unit.

In the first mentioned arrangement, the plurality of strands are simultaneously fed by separate feed rolls to the melting chamber, preferably through separate guides, and at a rate determined by the predetermined proportions in the finished product. In the second arrangement, a single set of feed rolls supplies the unitary, multi-material rod or wire to the melting chamber, this rod or wire comprising a cored element having concentric layers of the different materials, or a stranded element comprising a plurality of complementary sectional strands cooperating to form a circular-section unitary element, and the like. The higher melting metal or materials is preferably fed to the hottest portion of the melting chamber. For example, in the cored rod, the higher melting material forms an envelope for the lower melting material.

In order that a good bond may be procured between the surface upon which the composite metal is to be laid, it is usually necessary that the surface be first prepared, either by a "thermit" type flux, or by heating it to bonding temperature during the spraying operation, which may be done with the spray or the flame issuing from the nozzle, depending upon the position of the surface with respect to the nozzle, or by separate heating means, or by both of these methods.

It will be seen that with the new method of this invention, many materials, otherwise unmiscible in liquid state, may be combined mechanically, and numerous novel and useful composite structures, having unique physical properties resulting from the aggregate of the physical properties of the individual materials, may be provided, and, by a predetermined composition of gaseous conveying envelope, one or more of the materials may be altered in their ultimate physical or chemical structures.

For a more complete understanding of the invention, reference may be had to the accompanying drawing, in which:

Figure 1 illustrates, in partial section, the preferred apparatus for simultaneously spraying a plurality of molten materials according to the method of this invention;

Figs. 2 and 3 illustrate in perspective two forms of a cored rod formed of two or more metals for use in the apparatus;

Fig. 4 illustrates, in partial section, a modified form of the apparatus.

Assuming that a copper-lead bearing is to be made according to the present invention, a cored rod 10 such as is shown in Fig. 2 is prepared, the low melting metal, namely, lead, or an alloy predominantly lead, forming the core 12, while the higher melting metal, namely, copper, or an alloy predominantly copper, forms the tube or sleeve 13 enclosing the lead core 12. The cross-sectional area of the lead core 12 and the copper sleeve or tube 13 are predetermined in accordance with the proportion of copper and lead desired in the finished product. For example, if the finished product is desired to be a mixture of equal parts of lead and copper, the cross-sectional areas of the lead core 12 and the tube or sleeve 13 are predetermined accordingly. With this proportional arrangement of the two metals, the rod 10 can be fed by suitable means to the melting chamber and the predetermined proportion of the lead and copper is deposited on the target or other surface upon which the composite metal is to be laid.

In the rod 11 illustrated in Fig. 3 the lead core 14 is surrounded by two substantially semi-circular strands 15 of copper which are fed simultaneously with the lead core 14 so as to form a tube or sleeve around it in the manner illustrated. In this arrangement a third metal or material may be added simply by making one of the semi-circular strands 15 of such third metal or material. Likewise, the strands 15 may be made of segments less than a semi-circle if a fourth metal is to be included, and so on. Similarly, the rod may be composed of triangular segments jointly forming a rod.

As is illustrated in Fig. 1, the rod 10 or 11 may be conveniently fed to the melting chamber by a drive mechanism comprising two conical rolls 16 and 17, one of which, 16, is an idler, and the other, 17, is mounted on a shaft 18 which is driven from a suitable source of power preferably at constant speed. Details of a suitable driving mechanism for the shaft 17 are illustrated and described in copending application Serial No. 756,076, filed December 5, 1934, by Purling A. Bleakley. The cored rod, such as 10, is inserted through a guide thimble 19 which guides it between the feed rolls 16. Thimble 19 is adjustable laterally so as to change the position of the rod 10 with respect to the feed rolls 16 and 17, whereby the rate of the feed thereof may be varied at will to conform to requirements.

Suitably secured to the housing 20 in which the feed rolls 16 and 17 are located is a conical extension 21 carrying at its outer end the spray head 22 containing the melting chamber 23, which is a substantially closed chamber having a restricted orifice 24 substantially less in diameter than the maximum dimension of the melting chamber 23 and smaller in diameter than the chamber 25.

In operating the apparatus according to the method of the invention, the cored rod 10 is fed into guide funnel 25', through tube 26 and into the chamber 25 simultaneously with the oxy-acetylene or other high combustible fluid mixture, the combustion of which at upwards of 6000° F. progressively melts off the advancing end of the rod 10 within the melting chamber 23. The copper or higher melting metal, being located outside of the lead or lower melting metal, receives the full fusing heat of the flame first and the lead next, although in actual practice there is a simultaneous melting of the two metals.

As illustrated in Fig. 4, which, although embodying a modification of the apparatus for practicing the invention, nevertheless is provided with the same gas supply and mixing means as the arrangement of Fig. 1, with the section taken at right angles to that of Fig. 1, the acetylene, butane or other high temperature fluid is supplied by pipe 41, regulated by an adjustable needle valve 42, conducted by passage 43 to the opposite side of the head 22, into the center passage of needle valve 44 through cross passage 45 to passage 46' leading to turbulence chamber 28. The oxygen is supplied by pipe 46, is regulated by needle valve 44 and flows into passage 46', where it joins the acetylene in its course to be thoroughly mixed in turbulence chamber 28, which is a plurality of diagonal passages as illustrated in greater detail in aforementioned application Serial No. 756,076.

Owing to the difference in specific gravity of the acetylene and oxygen which tends to make them separate, insufficient oxygen is passed by valve 44 to support combustion of all of the acetylene passed by valve 42, the remainder of the oxygen necessary to complete combustion being supplied in the chamber in the manner to be described. The thorough oxy-acetylene mixture is maintained in baffle chamber 29 and it issues in thoroughly mixed condition into the chamber 25 through a plurality of passages or annular space 27.

Because the melting chamber 23 is substantially a closed chamber, the pressure within it builds up considerably and the temperature therein is maintained substantially equal to the temperature of the oxy-acetylene flame, namely, upwards of 6000° F., at which lead and copper are in supermolten condition inasmuch as the lead melts at approximately 625° F., and the copper at approximately 1930° F. The lead is prevented from vaporizing, probably because of the pressure within the combustion chamber 25.

The combustion-supporting air is supplied to the chamber 25 through passages 30 at proper pressure and in proper volume, determined by the metering ports 31, which are drilled passages of predetermined diameter and which pass air to chamber 34, to which it is supplied by passage 33 from a suitable source.

Air from chamber 32 also flows through passages 35 in a thin film under pressure over the interior surface of the melting chamber 23,

thereby cooling the nozzle 36 so that it is not hot to the touch even though the temperature in the center of the melting chamber is in excess of 6000° F. This air issues at considerable velocity from the orifice 24 in the form of a tubular envelope so as to not only comminute or atomize and convey the molten metals in a finely-divided, mixed state out of the combustion chamber 23, but also to maintain the molten metals at a pressure which precludes the metals, particularly the lead, from vaporizing during their travel from the combustion chamber 23 to the target or surface to which the composite metal is to be applied, such as a steel or other metal plate 37.

Depending upon the character of the metals being deposited, the distance of the plate 37 from the nozzle 36 varies from three to eighteen inches. The velocity of the molten metals is high and the temperature thereof is preserved by the high pressure tubular gaseous envelope so that it remains plastic up to the time that it is deposited upon the plate 37 or up to the time that it is deposited upon a previous layer of the metal, both this previous layer of metal and the surface of the plate being heated to a temperature such that the particles of the metal are welded to each other and to the plate 37. The velocity with which the particles strike the plate 37 assists materially in obtaining this close bond or weld.

The surface of the plate may be heated to bonding temperature by the molten metal spray, or by the flame issuing from the nozzle 24, depending upon its position with respect to the nozzle by separate heating means, or by a spray-ignitible flux on the surface, such as aluminum powder or a "thermit" mixture, and the like. Sal ammoniac and other fluxes for non-ferrous metals have been employed with success to secure a good bond between the surface and the sprayed metals. These fluxes are applied in dry or paste form to the surface of plate 37. The thermit mixtures appear to aid in roughening the surface 37 upon combustion. Also, in order to secure more rapid solidification of the composite mixture, the plate 37 may be made of copper or other good thermal conducting material to rapidly dissipate the heat of the deposit metal or material.

It has been found that in order to maintain the two metals, such as copper and lead, in their original state of purity, and to secure a strong, well-bonded structure, a volume of a third gas such as hydrogen or a reducing gas is preferably introduced at 39, metered through metering port 40, and mixed with the air in chamber 32 so as to neutralize the oxygen in the gaseous air envelope, probably by combining with the oxygen. In fact, it has been found that the best copper-lead structure can be obtained on plate 37 by incorporating in the air envelope a supply of hydrogen in the manner described. Similarly, other gases such as acetylene can be added to the air envelope or the entire envelope may be formed of a neutral gas such as nitrogen, or may constitute or include a gas which reacts with the metals being deposited, reduces it, or otherwise changes the mechanical or physical form of the deposited metal. The selection of the third gas in the air envelope or the constitution of the envelope is determined by the nature of the metals being deposited and the requirements as to their treatment during the time that they are in the molten state.

The same process is carried out with a cored rod of the type shown in Fig. 3 whether or not this rod comprises two, three or more metals. Although the proportion of the deposited metals is determined in the preferred process of this invention by properly proportioning the cross-sectional areas of the rod 12 and its sleeve or jacket 13, it will be understood that the separate strands of different metals may be fed to the melting chamber 23 at different rates by separate feeding means and in that way the proportions of the metals in the finished product predetermined.

For example, as illustrated in Fig. 4, the parts 47 and 48 are provided with two or more passages through which wires 49 and 50, differing in composition, are supplied to the chamber 25 for simultaneous melting in the melting chamber 23 in the presence of combustion-supporting air from 30, and for atomization, mixing and conduction to the place of deposit by the aforementioned gaseous envelope issuing from passage 36 and flowing out of nozzle aperture 24. The wires 49 and 50 are separately fed by independent sets of conical feed rolls 51 and 52, respectively, the shafts 53 and 54 which are preferably driven from a constant speed source. The respective guide thimbles 55 and 56 for the wires 49 and 50 are adjustable in the manner described for positioning the wires with respect to their feed rolls to obtain a speed commensurate with the volumetric proportions of the materials desired in the finished product.

Thus, wires of standard size but of different materials may be fed at different rates to the melting chamber. Also, three or more passages may be supplied in parts 47 and 48 for three or more wires, and the speed of shafts 53 and 54 may be varied instead of employing the conical feed rolls 51, 52 with adjustable thimbles 55, 56. Wires of different compositions may be twisted together into a cable, or otherwise bound together, preferably with the higher melting materials outside, and the cable fed to the melting chamber.

The composite structure 41 of copper and lead on a base 37 may be shaped into a bearing, with the base 37 shaped into a sleeve and the copper-lead structure 41 into the liner. Other structures have different uses, depending upon their compositions and physical or chemical properties. The texture and thickness of the deposit 41 is determined by the distance of the surface 37 from the nozzle opening 24, the materials being deposited, the composition of the gas envelope and the rate of relative movement between the nozzle and the plate 37. The plate 37 may be moved relatively to the apparatus as indicated by the arrow in Fig. 1, or the apparatus may be mounted on a pivot, in guides, or on rails for movement relatively to the work. The thickness of the structure 41 may be increased by continued application of the spray or by numerous passages thereof back and forth.

Although several preferred apparatus for practising the method of this invention have been illustrated and described herein, it is to be understood that the invention is not limited thereby, but is susceptible of changes in form and detail within its scope. Furthermore, although only certain materials, principally metals, have been mentioned as miscible according to the method of this invention, it is to be understood that the method may be employed for mixing metals and non-metals which melt, become plastic, or comminute or atomize in unmolten form, and the like, such as cements, graphite or carbon com-

E 831

pounds, glass, porcelain, sulphur, etc., any one or more of which may be mixed with nickel, copper, steel, etc., it being only necessary to properly proportion them and arrange them so that they can be fed to the melting space in the manner described.

I claim:

1. The method of forming a composite structure of at least two different metals, one of which normally vaporizes at the melting point of the other metal, which comprises supplying the metals to a melting chamber for joint melting therein, melting said metals in said chamber while maintaining therein a superatmospheric pressure sufficient to prevent vaporization of such metals and conveying said metals from said chamber and maintaining them under a pressure precluding vaporization thereof during their travel from the melting chamber to the place of deposit.

2. The method of forming a composite structure of at least two different metals, one of which normally vaporizes at the melting point of the other metal, which comprises supplying the metals to a melting zone for joint melting therein, melting said metals in said zone while maintaining therein a superatmospheric pressure preventing vaporization of said metals and conveying the fused metals simultaneously out of the melting zone to the place of deposit with a gaseous carrier stream under a pressure precluding vaporization thereof.

PURLING ALLEN BLEAKLEY.

Patented Feb. 27, 1945

2,370,242

UNITED STATES PATENT OFFICE

2,370,242

REFRACTORY METAL COMPOSITION

Franz R. Hensel and Earl I. Larsen, Indianapolis, Ind., assignors to P. R. Mallory & Co., Inc., Indianapolis, Ind., a corporation of Delaware

No Drawing. Application January 15, 1943, Serial No. 472,482

4 Claims. (Cl. 75—22)

This invention relates to metal compositions and articles made therefrom.

An object is to improve metal powder compositions.

Another object of the invention is to improve powder metal bodies such as electric contacts, welding electrodes, welding dies, current carrying bearings or bushings, valve seats and the like.

Other objects of the invention will be apparent from the description and claims.

The present invention contemplates a metal composition made from refractory metal powders, particularly tungsten and molybdenum, which are individually coated with protective layers of a palladium-platinum group metal such as platinum, palladium or rhodium and are bonded together in a metal composition with a metal from the first group of the periodic table such as copper, silver or gold.

The refractory powder may vary in average diameter between 0.5 and 100 microns prior to coating and the coating of protective metal such as platinum, palladium or rhodium may vary in thickness from a fraction of a micron to several thousandths of an inch. Thus the relative percentages of refractory metal or compound and protective metals in the coated powders used for producing the metal composition of the present invention may fall within the following range of proportions:

	Percent
Refractory metal	99.99 to 10
Palladium-platinum group metal	0.01 to 90

The coated powders are interspersed and bonded with the second group metal and the resulting compositions may fall within the following range:

	Percent
Coated tungsten or molybdenum powders	5 to 99
Copper, silver or gold	Balance

This range may be divided into two general classes of materials, namely:

Predominantly refractory compositions containing—

	Percent
Coated refractory powders	50 to 99
Copper, silver or gold	Balance

Predominantly low melting point metal compositions containing—

	Percent
Coated refractory powders	5 to 49.9
Copper, silver or gold	Balance

Following are several examples of suitable metal compositions:

	Percent
(a) Molybdenum particles coated with rhodium	50
Silver	50
(b) Molybdenum particles coated with rhodium	60
Silver	40
(c) Tungsten particles coated with rhodium	65
Silver	35
(d) Tungsten particles coated with rhodium	50
Silver	50
(e) Tungsten coated with rhodium	80
Silver	20
(f) Molybdenum particles coated with platinum and/or palladium	50
Silver	50
(g) Molybdenum particles coated with platinum and/or palladium	60
Silver	40
(h) Tungsten particles coated with platinum and/or palladium	65
Silver	35
(i) Tungsten particles coated with platinum and/or palladium	50
Silver	50
(j) Tungsten coated with platinum and/or palladium	80
Silver	20
(k) Tungsten coated with platinum and/or palladium or rhodium	45
Gold	55
(m) Tungsten coated with platinum and/or palladium or rhodium	70
Copper	30
(x) Tungsten coated with platinum and/or palladium or rhodium	50
Copper	50

The protective coating of rhodium, platinum or palladium may be applied by any one of several methods such as electroplating, cathode sputtering, metal spraying, condensing evaporated metal on the particle surfaces, chemical deposition. They may also be coated by first coating the powders with a dispersible adhesive, then dusting the adhesive coated particles with the protective metals in powder form and subsequently heating the coated powders to disperse the adhesive and diffusing the protective metal onto the surfaces of the refractory powders. It is also possible to use a metal paste as a coating medium.

The metal compositions of the present invention may be made from the coated particles in several ways. The coated refractory particles, or a mixture of them, may be pressed to form a powder compact and the compact then sintered at a suitable temperature such as 1200° C. to form

E 833

a sinter-bonded metal body. This body is then impregnated with silver, copper or gold or any alloy of two or more of these, by placing the first group metal in contact with the sintered compact and heating the assembly in a reducing atmosphere to a temperature above the melting point of the lower melting metal so that it will flow into the pores of the sintered body and fill them.

The metal composition may also be produced by mixing the coated particles directly with powders of copper, silver or gold, or mixtures of these, pressing the mixed powders and then sintering the pressed mixture at a suitable temperature such as 950° C. to produce the finished composition. If desired, subsequent repressing or coining operations may be applied to further increase the density and improve the physical characteristics of the composition.

A third method of manufacture comprises a combination of the above two methods. According to this method, a portion of the copper, silver or gold in the form of a powder is mixed with the coated refractory powders and the mixture pressed in a suitable die. The pressed body is then sintered at a temperature to cause binding, such as 1250° C. Additional amounts of copper, silver or gold are then placed in contact with the sintered body and the assembly heated to a temperature above the lower melting point metal to cause impregnation.

During the sintering operation, according to any of the above methods, the protective layers of platinum, palladium or rhodium on the refractory metal particles diffuse into the refractory material to a greater or lesser extent, forming alloys or compositions at the surfaces of the particles. These surface layers are considerably more noble in character as far as oxidation is concerned than the refractory particles themselves. The degree of diffusion of the protective metal will depend upon the time and temperature of the sintering process. It is also contemplated that in some cases the coated powders may be pre-sintered in the loose state to accomplish diffusion before the powders are used in manufacturing the metal composition.

An advantage of the present composition and process resides in the affinity between the first group metals such as copper, silver and gold and the protective metals such as palladium, platinum or rhodium. Since the first group metals have a tendency to alloy with the protective layers they are readily drawn into any pores or spaces in the metal compact resulting in a denser and more nearly perfect and homogeneous metal structure. The alloying also produces a strong bond between the various metal phases present.

In some cases additions of small proportions of other ingredients may be made to the compositions. For instance, from a fraction of a per cent to 10% of carbon or boron may be added to the mixture. The carbon is preferably in the form of graphite.

Such elements as nickel, cobalt, iron, manganese or silicon may be added in proportions ranging from a fraction of 1% to 30%. These have the effect of increasing the hardness, wear resistance and tensile strength of the compositions.

One important use of the metal compositions of the present invention is in electric contacts. Electric contacts have heretofore been produced of compositions of refractory metals and compounds with silver and copper in various proportions. However, such compositions have developed relatively high contact resistances between the contacting surfaces and have exhibited a substantial temperature rise when subjected to continuous operation. The use of a protective metal coating from the palladium-platinum group on the refractory particles reduces the contact resistance considerably and produces a contact much less subject to overheating.

By using contacts formed of the compositions described on one or both sides of a contact pair, sticking and high contact resistance can be eliminated in most cases.

Refractory compositions of the present invention which are particularly suitable for cooperation with cadmium oxide contacts of the type described in Hensel Patent 2,145,690 are coated molybdenum particles with silver, and coated tungsten with silver.

While specific embodiments of the invention have been described, it is intended to cover the invention broadly within the spirit and scope of the appended claims.

What is claimed is:

1. A metal composition formed of particles of refractory metal selected from the group consisting of tungsten and molybdenum, and a coating thereon of metal selected from the group consisting of palladium, platinum and rhodium and metal selected from the first group of the Periodic Table consisting of copper, silver and gold interspersed with and bonded to said coated particles.

2. A metal composition formed of particles of refractory metal selected from the group consisting of tungsten and molybdenum, and a coating thereon of metal selected from the group consisting of palladium, platinum and rhodium and metal selected from the first group of the Periodic Table consisting of copper, silver and gold interspersed with and bonded to said coated particles, said coated particles being formed of 99.99% to 10% of said refractory metal and .01% to 90% of said coating metal, the coated particles forming 5 to 99% of said composition and said first group metal forming the balance.

3. An electric contact formed of a metal composition composed of particles of refractory metal selected from the group consisting of tungsten and molybdenum, and a coating on said particles of metal selected from the group consisting of palladium, platinum and rhodium and metal selected from the first group of the Periodic Table consisting of copper, silver and gold interspersed with and bonded to said coated particles.

4. An electric contact formed of a metal composition composed of particles of refractory metal selected from the group consisting of tungsten and molybdenum, and a coating on said particles of metal selected from the group consisting of palladium, platinum and rhodium and metal selected from the first group of the Periodic Table, consisting of copper, silver and gold interspersed with and bonded to said coated particles, said coated particles being formed of 99.99% to 10% of said refractory metal and .01 to 90% of said coating metal, the coated particles forming 5 to 99% of said composition and said first group metal forming the balance.

FRANZ R. HENSEL.
EARL I. LARSEN.

E 834

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,775,531 December 25, 1956

Earle T. Montgomery et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 72, after "parts" insert -- formed --; column 4, line 11, for "an angle at 45°" read -- an angle as 45° --.

Signed and sealed this 2nd day of April 1957.

(SEAL)
Attest:
KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

E 835

United States Patent Office

2,775,531

Patented Dec. 25, 1956

2,775,531

METHOD OF COATING A METAL SURFACE

Earle T. Montgomery, Arnold P. Welch, and Joseph L. Bifonte, Columbus, Ohio, assignors to The Ohio State University Research Foundation, Columbus, Ohio, a corporation of Ohio

No Drawing. Application May 10, 1949, Serial No. 92,508

3 Claims. (Cl. 117—22)

The invention disclosed in this application relates in general to coatings for metals, and more particularly to processes for forming such coatings and for adhering such coatings to the metals to be coated; to articles comprising metals provided with such coatings; and to compositions of matter useful as such metal coatings. The embodiments of our invention disclosed in illustration thereof are particularly useful as coatings for withstanding high temperatures and protecting the coated metals at these temperatures; and the methods disclosed in illustration of our invention are particularly useful in forming such coatings and compositions, and in adhering such coatings and compositions to metals.

One of the objects of our invention is the provision of a new coating for metals which is not only resistant to high temperatures but also resistant to oxidation and is at the same time a thermal insulating coating.

A further object of our invention is the development of processes for forming such coatings and for adhering such coatings to the metal to be coated.

A further object of our invention is the provision of an article comprising a metal, having alloyed or sinter-bonded thereto, both a refractory and a heat and corrosion protective coating consisting of a sinter-bonded mixture of a metal or alloy and a ceramic component which may be, for example, a metal oxide.

Another object of our invention is the production of a new material or composition of matter with a combination of properties making it superior as a protective coating for metal (especially at high temperatures) to all coatings of the prior art, including the glass-type enamels.

Further objects and features of our invention will be apparent from the reading of the following specification and claims.

We have designated our compositions of matter as "Cermets" inasmuch as they consist of a bonded mixture of extremely small particles of a ceramic material, such as a metal oxide, and small particles of a metal or metal alloy.

The compositions of matter, useful as coatings, with which we are primarily concerned herein are therefore bonded mixtures of small particles of ceramic materials and small particles of metals or alloys. One example of such a cermet coating is a composition consisting of a mixture of powdered nickel metal and powdered magnesium oxide (magnesia). The magnesia is preferably the electrically fused variety which has the greatest density and therefore a minimum shrinkage. The mixture of nickel and magnesia can be pressed into compacts or briquettes and sintered to agglomerate and sinter-bond the components by a wetting reaction and solid solution between the metal and the ceramic component through the media of a limited oxide film formed on the nickel particles. Then the composition can be further prepared by crushing the compacts and screening the powder preparatory to flame-spraying. The coating composition is then ready for direct application to parts of sheet-metal, or other metal parts, by flame-spraying with an oxy-acetylene powder gun.

Alternatively, the raw and unsintered mixed powders alone; the sintered and ground powder alone; or a mixture of raw powder and sintered powder, may be applied to the metal part to be coated, by a different process. For example, the coating in one of these forms, may be initially adhered by cold application using a fluid vehicle such as a solution of sodium silicate in water, by any of the coating methods known to the art and commonly employed for the application of enamels, lacquers or paints. After drying the coating so initially applied, the coating may be torched with an oxyacetylene torch flame to agglomerate and sinter-bond the materials of which the coating is composed to each other and to the metal part, and preferably to alloy the metal or alloy component of the coating to the metal part being coated. The same results may be obtained by furnace sintering.

When the mild steels are to be coated by cold application of the coating, as described above, which application is to be followed by torching or furnace sintering, it has been found that the application of an undercoat of flame sprayed or electroplated nickel, or other oxidation resistant metal, onto the mild steel promotes better adherence because it inhibits the development of an oxide film on the mild steel at the interface between the steel and the coating, during the drying and subsequent torching or furnace sintering operation.

We prefer very much that the surface to be coated should be sand-blasted before applying the coating.

Of the many metals which are suitable for use in our process, we prefer nickel, cobalt, aluminum, and iron, or alloys of these metals. By listing only four metals we do not limit ourselves thereto. By the term "alloys of these metals" we do not intend to limit ourselves to inter alloys of the four metals mentioned, but we include alloys of any of these four or any other suitable metals with any of the others or with any suitable metal such as, for example, with chromium, columbium, tantalum, titanium, tungsten or zirconium. By "metals" we include any suitable metals or any suitable alloy of such metals and we so define the words "metal" and "metals" as used hereinafter in this specification and in the claims. Of the many metal oxides we prefer alumina, beryllia, magnesia, silica, and zirconia. We do not, however, wish to limit ourselves to the five oxides mentioned. We have tested more thoroughly than other coatings, those consisting of mixtures of magnesia and nickel. Of course, metals (e. g., chromium) other than those listed above, are also useful, and oxides and even other similar compounds (e. g., silicon carbide) other than the ones listed may also be useful as ceramics in our process of preparing coatings as also may be mixtures of suitable oxides. However, we prefer zirconia or magnesia as a ceramic component. The degree of usefulness of a given coating varies with the metal and ceramic component selected—and with the metal to be coated. The degree of usefulness varies in fact to a large extent depending on the degree with which the metal and the ceramic component selected, wet each other and in turn wet or alloy with the metal to be coated. The usefulness also varies with the temperature to which the coating is subjected in use. The greater the degree of wetting or agglomeration there is, the greater is the usefulness of the combination, provided the combination will also alloy with the metal to be coated, and is sufficiently refractory for a given service.

We have found that when we sinter-bond a mixture of fine particles of a metal and a ceramic component to a metal sheet, for example, we can produce a coating which will withstand much higher temperatures than have been previously possible with any coatings known in the prior

art and even higher than the temperatures which can be withstood by the metal itself. At the same time the coating protects the sheet from oxidation and corrosion; provides some thermal insulation, i. e., reduces the density of heat transfer; and increases the normal temperature differential between the heated and unheated surfaces.

In sinter-bonding or alloying the coating to the metal to be coated, we reduce the particle size of the presintered powder, and of both the metal component and the ceramic component comprising the cold coating mixture, to extremely small particles. The size of such particles is not critical, but for flame spraying, the material should be less than 325 mesh for the presintering operation and then after presintering, ground and screened to provide particles having a size of less than 100 mesh (149 microns) and greater than 325 mesh (44 microns), the screens used being U. S. Standard brass sieves. The material for cold application should be less than 325 mesh (44 microns and finer).

Then we adhere the mixture by flame-spraying or torching. In flame-spraying the material passes through the flame. In heating particles of such size to the temperatures attained by them in flame-spraying, the metal particles bonded to the ceramic component of the presintered powder, reach, we believe, the plastic or tacky stage in the oxyacetylene flame, while in torching a mixed sintered and unsintered powder, it appears that in many cases a film of the oxide of the metal component forms on the surface of the metal or alloy component and this metal oxide film goes into solid solution with the ceramic component. In other cases we believe that there is a sinter-bonded agglomeration only, without wetting or solid solution. Although the temperatures used are not necessarily critical for all mixtures, the optimum temperature being dependent on the components, yet we prefer usually to sinter at temperatures within ranges producing the conditions above referred to.

In bonding the particles to each other and to the metal to be coated, we use a variety of methods. We may flame-spray the presintered and ground mixture of metal component and ceramic component particles onto the surface to be coated. In so flame-spraying, we use a commercial "Powder-weld" oxyacetylene powder gun. In the case of this oxyacetylene powder gun or other similar types of high temperature torch guns, the flame may be surrounded with neutral nitrogen gas.

Alternatively, we may make an application of (1) presintered and ground coating alone, (2) a raw mixture of metal component and ceramic component particles, or (3) a combination of (1) and (2), by using a fluid vehicle, and spraying, brushing, dipping, or applying by any other usual means, and after drying, either torch the coating with an oxyacetylene torch flame to sinter-bond the materials of the coating and alloy or sinter-bond the coating to the metal part being coated, or accomplish the same results by furnace sintering.

In preparing the mixture of fine metal or alloy and ceramic component particles, we may grind the materials separately then mix them together prior to presintering in the form of a compact, or prior to applying them raw and unsintered as a coating. For flame-spraying, which is our preferred method of application, we presinter the mixture. To do so we grind the materials and mix them together and then form them into a briquette or compact by pressing (or otherwise) and sinter by heating the briquettes or compacts in a furnace, to a temperature which will agglomerate and/or sinter-bond the components. An oxidizing, neutral, or reducing atmophere may be used in the furnace depending on the composition and on whether or not a passivated skin is formed on the compacts. After sintering the compacts or briquettes, they are crushed to a fine powder of the order of less than 100 mesh (149 microns and finer) and greater than 325 mesh (44 microns) and then applied as the coating.

Direct flame-spraying of presintered powder, regardless of the character of the components, is the preferred method of applying the coating wherever the dimensions of the part to be coated with permit. In such process the presintered and ground powder is sprayed through a torch flame as for example an oxyacetylene torch, in such manner that the heated particles impinge on the surface being coated. For good adherence of the flame-sprayed powder, the angle of incidence should be as near 90° as possible, although good adherence can be obtained with as low an angle at 45°. There are often situations, however, where the dimensions of the part to be coated on its inner surface will neither permit the entrance of the gun with the necessary clearance for flame-spraying, nor permit spraying the interior at an advantageous angle from a position outside the part. In such cases, either for the reason just explained, for reasons of cost or practicability in building up thicker coats, or for adaptation to production line processing, we have recourse to the cold method of application of the coating, as described above, followed by torching with an oxyacetylene torch flame or by furnace sintering.

So far as we know, we are the first to produce refractory, protective, thermal insulating, and hard surface coatings for metals, said coatings consisting of a mixture of a metal or alloy powder (or flake) and a ceramic or non-metal powder. Adherence of the coating to the metal part to be coated is achieved, we believe, by an alloying reaction between the metal of the coating and the metal base. However, certain coating compositions will not alloy with certain metal bases and in such cases a purely mechanical adherence is achieved which is useful for applications where the part is not subject to thermal cycling.

This type of refractory coating has been developed particularly for service in a temperature range above that in which the glass-type enamel ground coats, and the glass-bonded refractory cover coats for enamels are useful. The plastic stage of the most refractory high temperature enamels is still below the plastic stage of the metals to which they can be applied. Also, enamels which can be applied at temperatures even as high as from 2300° to 2350° do not have an effective life even at temperatures of from 1800° F. to 2000° F.

The proportion of metal or alloy to ceramic material in the cermet coating depends to some extent on the materials. However, we prefer to use compositions within the range of a mixture having 25% metal and 75% ceramic material to a mixture having 75% metal and 25% ceramic material. One very satisfactory composition consists of 66.7% ground nickel and 33.3% ground electrically fused magnesia (both percentages by weight).

Following are specific examples of the practice of various embodiments of our inventions.

Example 1

Following is a description of our preferred method of preparing nickel-magnesia coating ±10 for flame-spraying; and a description of the spraying technique.

We obtained commercial electrically fused magnesia of the fineness of 325 mesh and finer (approx. less than 44 microns) and commercial nickel metal of the same fineness. We mixed together 200 grams (33.3%) magnesia and 400 grams (66.7%) nickel, by dry grinding together for 30 minutes in a steel ball mill with steel balls. After mixing, the powder was moistened with 8% water containing a small amount of an organic binder (such as for example a starch suspension). It was then pressed into compacts in a steel die, using approximately 12,000 p. s. i. After drying at 250° F. the compacts were introduced into a Globar furnace with normal oxidizing atmosphere, which had previously been brought to the temperature of 2550° F. The compacts were sintered by soaking at this temperature for 30 minutes. After cooling, the compacts were

crushed, the material was passed through a disc pulverizer, and screened in a Rotap machine using U. S. Standard screens 100 mesh and 325 mesh. The fraction which passed the 100 mesh screen but was retained on the 325 mesh screen, was used for flame-spraying by means of a "Powder-weld" oxyacetylene flame powder gun.

The metal surface to be flame-sprayed was cleaned and roughened by grit blasting using a sharp and fairly coarse silica sand or silicon-carbide grit. The coating was applied by the same technique as used for flame-spraying metal powders, which is well known to the art. The coating is accomplished without undue heating of the target (the metal part being coated). The temperature attained by the target is controlled by the distance from the gun to the target. Just enough heat is used to alloy a given coating to a given metal base.

Example II

As described in the specification, a cermet coating may be initially adhered to the metal part to be coated, by cold application in any one of three forms: (1) presintered and ground powder alone, (2) raw and unsintered mixed powders alone, or (3) a mixture of presintered powder and raw (unsintered) mixed powders.

Following is a description of our preferred method of preparing nickel-magnesia coating #10 for cold application, using a mixture of presintered powder and raw powder; and a description of the technique of application. We obtained commercial electrically fused magnesia of the fineness of 325 mesh and finer (approx. less than 44 microns) and commercial nickel metal of the same fineness. In addition we obtained by the process described under Example I, presintered #10 Ni-MgO coating material of the fineness of 325 mesh and finer. We mixed together 100 grams (16.7%) magnesia, 200 grams (33.3%) nickel and 300 grams (50.0%) presintered material of Example I, by dry grinding together for 30 minutes in a steel ball mill with steel balls. After mixing, the powder was brought to the consistency of a slurry by stirring with a 30% sodium silicate solution and then brushed on the article to be coated, the surface of which had been cleaned and roughened by sandblasting. The coating, so applied, was dried by infra-red radiation and finally in a conventional drier at 250° F. We then matured the coating through agglomeration and sinter-bonding, and alloyed it to the metal part being coated by torching the coated surface with an oxyacetylene torch flame within the range 2100° F. to about 2500° F. Alternatively, this coating, as here described, has been initially applied by spraying instead of brushing, using a conventional glaze or enamel gun.

Example III

Following is a description of the preparation of one composition of our aluminum-alumina coating for flame-spraying.

We obtained commercial calcined alumina reduced to particle size of about 44 microns and finer, and commercial aluminum flake reduced to a thickness of about 5 milli-microns. We mixed together 150 grams (50%) alumina and 150 grams (50%) aluminum in a porcelain mortar. After mixing, the material was dampened with 10% water containing a small amount of organic binder and pressed into compacts, using approximately 1200 p. s. i. These were dried slowly to 600° F. and sintered by placing in a furnace having a normal oxidizing atmosphere which had previously been brought to a temperature of 2500° F., and then soaking the compacts in this furnace for 8 minutes to agglomerate and sinter-bond the components. In sintering these compacts as here described, a tight and passivated skin of aluminum oxide forms on all surfaces of the compact, leaving the metal content of the interior in the metallic state. The compacts were then crushed, ground, and screened as described under Example I. The fraction which passed the 100 mesh screen but was retained on the 325 mesh screen, was used for flame-spraying as described under Example I.

Example IV

Following is a description of our preferred method of preparing nickel-zirconia coating for flame-spraying.

We obtained commercial fused, stabilized zirconia of the fineness of 325 mesh and finer (approx. less than 44 microns) and commercial nickel metal of the same fineness. We mixed together 200 grams (33.3%) zirconia and 400 grams (66.7%) nickel, by dry grinding together for 30 minutes in a steel ball mill with steel balls. After mixing, the powder was moistened with 8% water containing a small amount of temporary binder: It was then pressed into compacts in a steel die, using approximately 12,000 p. s. i. After drying at 250° F., the compacts were sintered by placing in a furnace having a normal oxidizing atmosphere and which had previously been brought to a temperature of 2550° F., and then soaking the compacts in this furnace for 30 minutes to agglomerate and sinter-bond the components. The compacts were then crushed, ground, and screened as described under Example I. The portion which passed the 100 mesh screen but was retained in the 325 mesh screen, was used for flame-spraying as described under Example I.

Example V

Following is a description of our preferred method of preparing cobalt-magnesia coating for flame-spraying.

We obtained commercial electrically fused magnesia of the fineness of 325 mesh and finer (approx. less than 44 microns) and commercial cobalt metal of the same fineness. We mixed together 200 grams (33.3%) magnesia and 400 grams (66.7%) cobalt, by dry grinding together for 30 minutes in a steel ball mill with steel balls. After mixing, the powder was moistened with 8% water containing a small amount of temporary binder. It was then pressed into compacts in a steel die, using approximately 12,000 p. s. i. After drying at 250° F., the compacts were sintered by placing in a furnace having a normal oxidizing atmosphere which had previously been brought to a temperature of 2550° F., and then soaking the compacts in this furnace for 20 minutes to agglomerate and sinter-bond the components. The compacts were then crushed, ground, and screened as described under Example I. The portion which passed the 100 mesh screen but was retained on the 325 mesh screen, was used for flame-spraying as described under Example I.

In addition mixtures of nickel and zirconia and mixtures of cobalt and magnesia have each been used separately to form nickel-zirconia or cobalt-magnesia coatings by cold application in a manner analogous to that described under Example II.

It is to be understood that the above described embodiments of our invention are for the purpose of illustration only and various changes may be made without departing from the spirit and scope of our invention.

We claim:

1. A process of plating a metal surface which comprises forming small particles of metal selected from the group consisting of aluminum, iron, nickel and cobalt, forming small particles of a metal oxide selected from the group consisting of alumina, magnesia and zirconia, mixing the metal and the metal oxide particles together, sintering said mixture, reducing the sintered mixture to particles of powder of extremely small size, and flame-spraying the mixed sintered particles on the surface to be coated and thereby heating said particles of powder to a sintering temperature of at least approximately 2100° F.

2. A method of forming a heat resisting coating for a metal surface in which fine particles of metal selected from the group consisting of aluminum, iron, nickel and

cobalt and fine particles of a metal oxide selected from the group consisting of alumina, magnesia and zirconia are ground to size of less than 40 microns, formed as a mixture into a compact mass, sintered, reground to an average size of about 40-150 microns, and flame-sprayed onto the metal surface to heat said sintered and reground mixture to a sintering temperature of at least approximately 2100° F. in the order stated.

3. A process of coating a metal article which comprises forming a mixture of fine particles of a metal selected from the group consisting of aluminum, iron, nickel and cobalt and of a metal oxide selected from the group consisting of alumina, magnesia and zirconia, sintering said mixture, reducing the sintered article to particles of powder of extremely small size and flame-spraying the powder onto the surface of the article by an oxyacetylene flame with a sheath of neutral gas surrounding the oxyacetylene flame to heat the particles of powder to a sintering temperature of at least approximately 2100° F.

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METHOD OF PRODUCING COMPOSITE METAL POWDERS

Filed April 11, 1956

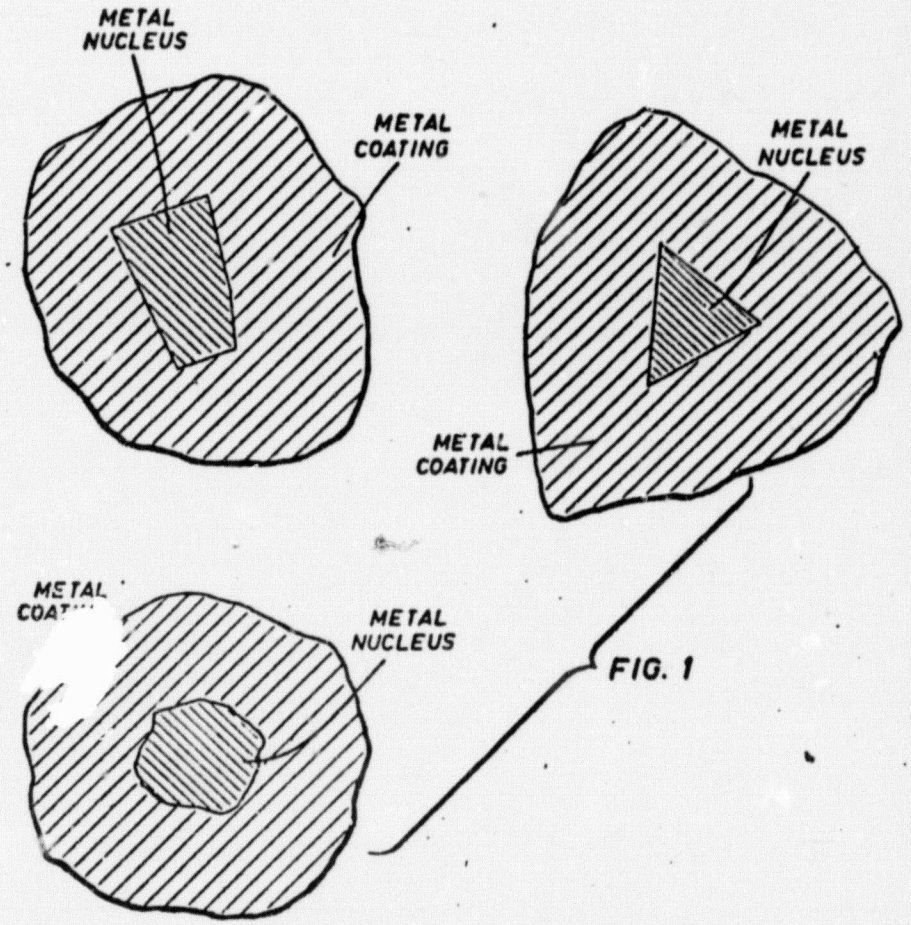

FIG. 1

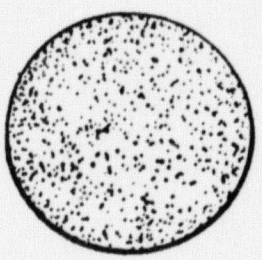

FIG. 2

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United States Patent Office E 840 2,853,403
Patented Sept. 23, 1958

2,853,403

METHOD OF PRODUCING COMPOSITE METAL POWDERS

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Application April 11, 1956, Serial No. 577,443

7 Claims. (Cl. 117—100)

This invention relates to a method of producing composite metal powders. The method is particularly directed to producing finely divided composite metal particles comprised of two or more metals having different chemical and/or physical properties by dispersing, in solid form, particles of one or more metals of interest as nuclei in an ammoniated solution in which another metal of interest having different chemical and/or physical properties is present as a soluble salt, and precipitating the latter metal from the solution by gas reduction to form composite metal particles in which the dispersed metal particles are coated by the precipitated metal.

The use of composite metal powders having different chemical and/or physical properties is well known and they are widely used in industry as such or in the form of compacts, particularly in powder metallurgy. Composite metal powders are used, for example, in alloying in the manufacture of special metal parts, especially small metal parts which cannot be manufactured satisfactorily, conveniently, or economically by conventional melting and casting methods. Also, composite powders in which one metal is coated with a film or coating of a metal having different physical and/or chemical properties are well known and are in widespread use, also in the powder metal industry. Also well known and of increasing importance in the latter industry are prealloyed powders in which two or more metals are mixed on an atomic rather than on a macroscopic scale.

Heretofore, composite metal powders have been produced by spraying or sputtering the metals of interest at a temperature above the melting temperature and/or by mechanical attrition and/or by mechanically mixing powders prepared separately. Production of metal powder by spraying is restricted to metals having low melting temperatures and the size of the resulting particles varies over a wide range. Mechanical attrition is slow, costly, and involves the use of fine grinding apparatus such as rod mills, plates, and ball mills, all of which require special, costly grinding media and/or lining. In addition, such methods have the further disadvantage in that they tend to contaminate the purity of the resulting product with particles of the grinding media or of the lining and there is a real danger of oxidation during the comminuting treatments.

We have found that problems heretofore attendant with the production of composite powders can be overcome very easily and very inexpensively. In its simplest form, the method of the present invention contemplates the dispersion, in solid form, of particles of a metal, or of two or more metals, in an ammoniated solution which contains, in solution, a soluble salt of a metal which can be precipitated from the solution as a metal powder by reaction with a reducing gas at elevated temperature and pressure. The mixture of dispersed and precipitated metal particles is agitated sufficiently to hold the dispersed metal particles in suspension in the solution. The temperature of the mixture is increased to and maintained at that temperature at which optimum reduction

is obtained and reducing gas is fed into the reaction vessel at a rate sufficient to establish and maintain the partial pressure of reducing gas at which reduction proceeds satisfactorily. The reducing reaction is continued until the dissolved metal salt content of the solution has been reduced to and precipitated as metal powder to the desired extent. The resulting product, in the form of an intimate association of metal particles having different chemical and/or physical properties is separated from the solution, such as by filtering. It is washed and dried and is then in ideal condition for use as such or as a compact prepared by conventional methods.

The term "dispersed metal" used herein is intended to include particles of one or more metals of the group copper, silver, gold, beryllium, zinc, cadmium, boron, aluminum, indium, titanium, germanium, zirconium, tin, hafnium, lead, vanadium, niobium, antimony, tantalum, bismuth, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, uranium and thorium. Such "dispersed metals" must be substantially insoluble in ammoniated solution under reducing conditions. They are employed as nuclei in the solution on which precipitated metal can deposit and grow as the reduction proceeds. Thus, the "dispersed metal" particles or nuclei preferably are of a particle size such that they can be held in suspension in the solution during reduction. A preferred particle size is within the range of from about 200 to about 1 micron or smaller.

Metal values which can be precipitated from an ammoniated solution by reaction with a reducing gas at elevated temperature and pressure are those of the group osmium, rhodium, ruthenium, iridium, gold, platinum, palladium, silver, copper, arsenic, tin, nickel and cobalt. Usually, however, these precipitatable metals will be of the group silver, copper, nickel and cobalt. These metals can be precipitated in metallic state as metal powders from an ammoniated solution very rapidly by reaction with a reducing gas at elevated temperature and pressure.

The preparation of composite metal powders containing two or more of the above described group of precipitatable metals can be produced very easily according to the method of the present invention by preparing an ammoniated solution containing dissolved salts of two or more of the desired metals. Reduction is conducted to precipitate first the most easily reduced metal, which is retained in suspension in the solution by agitation. Reduction is then continued to precipitate the next metal in the order of its reducibility. The order of precipitation from an ammoniated solution containing two or more precipitatable metals can be determined readily by the positions of the respective metals in the electromotive series of the elements. For example, the reducibility of the metals silver, copper, nickel and cobalt from an ammoniated solution is in the order named. "Dispersed metals" or nuclei which cannot be precipitated from an ammoniated solution by gas reduction must, of course, be prepared in the desired particle size by known or conventional methods prior to their dispersion in the solution.

The method is conducted very simply. Particles of the "dispersed metals" or nuclei of a particle size such that they can be suspended by agitation in the solution undergoing treatment are dispersed in the ammoniated solution to form a slurry. The metal having physical and/or chemical properties different from those of the "dispersed metal" or nuclei which is to be precipitated from the solution is present in the solution as soluble salt. Factors which affect the reduction and precipitation of metal values from the solution are the nature and characteristics of the metal to be precipitated, the temperature and pressure at which the reducing reaction is conducted, the

nature and the characteristics of the solution and the reducing gas employed. All these factors must be taken into consideration and the conditions of operation adjusted to produce optimum precipitation of the desired metal as metal powder.

The desired ratio of the respective metals in the desired composite metal can be obtained very easily. Under normal conditions, dissolved metal values in the ammoniated solution can be reduced to about 1 gram per litre very easily and very rapidly. Thus, it is only necessary to add to the solution a slight excess of the metal values to be precipitated, of the order of about 1 gram per litre, and the desired amount of "dispersed metal" particles. For example, if it is desired to produce a composite metal powder containing about 500 grams of molybdenum and 50 grams of cobalt, the prescribed amount of molybdenum is dispersed in, for example, a litre of an ammoniated solution which contains about 51 grams of cobalt and suspended therein by active agitation. Reduction is continued until only about 1 grame of cobalt remains in the solution. If it is desired to form a composite metal powder comprised, for example, of 70% nickel and 30% copper, an ammoniated solution can be prepared which contains the desired ratio of metals as soluble salts. The solution is then reacted with a reducing gas such as hydrogen at elevated temperature and pressure. Copper precipitates first as metal powder and is retained in suspension in the solution by agitation during precipitation of nickel metal powder. Reduction is continued until the nickel content of the solution has been reduced to the desired extent. The resulting composite metal powder, after separation from the solution, washed and dried, contains the desired nickel to copper ratio.

The solution is selected with regard to the solubility therein of the dispersed metal particles and the metal values to be precipitated and the reactivity of the reducing gas employed. Thus, the solution can be organic or inorganic, acid, basic or neutral, having regard to all the factors entering into the reduction.

Usually, the solution to be treated will be an aqueous ammoniated sulphate or chloride solution.

Ammonia usually is preferred as the complex forming ammine. However, organic ammines such as methyl amines or ethylene diamine can be substituted for all or part of the ammonia.

The reducing gas also is selected with regard to all factors entering into the reducing reaction. Usually, it will be desired to precipitate metals from the solution substantially free from impurities. It is preferred to employ hydrogen as the reducing agent in the precipitation of pure or substantially pure metal from the solution. However, other reducing gases such as carbon monoxide, methane, producer gas, natural gas or mixtures of reducing gases can be employed, if desired.

The anion of the metal to be precipitated is selected with regard to the solubility of the metal salt in the selected solvent and the reactivity of the anion with the reducing gas. Usually, in basic solutions, sulphate, chloride, carbonate and hydroxyl anions and in acid solutions sulphate, fluosilicate or acetate anions can be employed.

The time required for the reducing reaction is a function of the temperature and the pressure at which the reaction is conducted and varies inversely therewith. Preferably, the reaction is conducted at a temperature within the range of from about 250° F. to about 500° F. The reaction can be conducted at a temperature below about 250° F. but it tends to proceed too slowly for large scale commercial operation. Also, the reaction can be conducted at a temperature above about 500° F., but the increased rate of reduction does not warrant the increased cost of the high temperature-high pressure equipment required.

The reducing reaction usually is conducted under a partial pressure of reducing gas above about 50 pounds per square inch, and preferably from about 100 to about

500 pounds per square inch, to produce a total pressure of from about 150 to 1000 pounds per square inch, preferably, from about 250 to 700 pounds per square inch. At partial pressures below about 50 pounds per square inch the reaction proceeds too slowly and the increased rate of the reaction above about 500 pounds per square inch usually does not warrant the cost of the high pressure equipment involved. The term "total pressure" is intended to means the pressure autogenously produced by the temperature at which the reducing reaction is conducted plus the partial pressure or the overpressure of the reducing gas employed.

The concentration of the metal salt in the solution is adjusted to that from which there is rapid precipitation of metal values from the solution but safely below that at which there would be any danger of crystallization in the reaction vessel or in pipe lines, valves, and pumps. For example, in the precipitation of copper as powder metal from solution by gas reduction, copper sulphate is quite soluble in aqueous acid or basic solution, up to about 100 grams per litre of copper at ambient temperature and to a greater extent at higher temperatures. Therefore, concentrations of up to 75 to 100 grams of copper as sulphate per litre can be employed safely. Similarly, nickel and cobalt sulphates are relatively highly soluble in ammoniacal solution and while it is preferred to employ solutions containing about 50 grams per litre, concentrations up to about 75 grams per litre of metal can be employed safely.

In the precipitation of metals from solution by gas reduction, certain metals, such as silver and copper do not require a hydrogenation catalyst to initiate and promote the reducing reaction. Other metals, such as nickel and cobalt require a hydrogenation catalyst. Thus, in the precipitation of nickel and cobalt from solution by gas reduction, it is necessary to provide a hydrogenation catalyst. In certain instances, the dispersed metal serves as a catalyst and it is not necessary to provide another catalyst or nucleating agent in the solution. Examples of metals which serve as a catalyst are iron, nickel, cobalt, molybdenum and titanium carbide. Metals such as chromium, however, do not act as a catalyst in the reduction of nickel and cobalt. In the absence of a catalyst, little or no reduction is obtained and it is necessary to provide it in the solution before initiating the reduction. There are a number of satisfactory addition agents which can be employed as catalysts or nucleating agents of which ferrous sulphate is preferred in the reduction of nickel and a mixture of sodium sulphide and potassium cyanide is preferred in the reduction of cobalt. The addition to the solution of 4 grams per litre or less of the preferred catalyst or nucleating agent is sufficient to initiate and promote reduction of nickel and cobalt from otherwise uncatalyzed solutions.

When precipitating metal powder from solution by gas reduction, the density of the resulting powder can be controlled by regulating the ammonia and/or the ammonium sulphate concentration of the solution. For example, copper metal can be precipitated from solutions of widely varying hydrogen ion contents. Accordingly, the solutions may range from strongly basic amine solutions containing much free ammonia or other amine to those containing relatively large amounts of free acid. It is found, however, that there should be the equivalent of from about 0.1 to 2.5 gram mols of ammonia present in the solution per gram atom of silver or copper or from about 1.5 to 4 gram mols ammonia per gram atom of nickel or cobalt or nickel plus cobalt in the precipitation of silver, copper, nickel and cobalt from solutions by gas reduction.

The desired mixture of metal powders is produced by forming a slurry comprised of the desired amount of dispersed metal particles or nuclei and an ammoniated solution containing, in the form of a soluble salt, the desired amount of metal to be precipitated. This slurry

is reacted in a reaction vessel, such as an autoclave, with a reducing gas at elevated temperature and under a partial pressure of reducing gas above the pressure autogenously generated by the temperature at which the reaction is conducted. The reducing reaction is continued until the desired amount of metal powder has been precipitated from the solution. At the end of the reduction period, the mixture of metal particles is separated from the solution, such as by filtration or by centrifuging, and is in ideal condition for use as such or for treatment by conventional means for forming a desired compacted product, such as by sintering and/or compressing according to known methods.

Resulting composite metal particles are illustrated in the accompanying drawing in which:

Figure 1 illustrates enlarged cross-sections through typical composite metal particles; and

Figure 2 is a top plan view of a compact formed of composite metal particles illustrated in Figure 1.

The composite particles were of a particle size of about 5 microns.

The following examples illustrate the operation of the present method to produce a mixture of metal particles coated with or otherwise intimately associated with other metal particles having different physical and/or chemical properties. In each example, hydrogen was employed as the reducing gas. The reducing reactions were conducted at a temperature of about 350° F. and under a partial pressure of hydrogen of about 100 pounds per [illegible] inch. A finite amount, less than about 4 grams per litre, of ferrous sulphate was added to the solution to promote the reduction of nickel and a finite amount, less than about 4 grams per litre, of a mixture of potassium cyanide and sodium sulphide was added to the solution to promote the reduction of cobalt. The dissolved metals were present in the ammoniated solution as sulphates. The solution contained, in addition to the dissolved salts, from about 0.1 to 2.5 gram mols of ammonia per gram atom of copper and from about 1.5 to about 4 gram mols of ammonia per gram atom of nickel or cobalt or nickel plus cobalt.

producing a composite powder from which a pre-alloyed powder can be obtained by a simple homogenizing heat treatment. Because of the intimate contact of the different metal surfaces, it is possible to press certain composite metal powders before homogenizing heat treatment and then utilize the sintering operation to obtain the desired degree of diffusion between the metals and thus produce the desired degree of alloy.

In other instances, it may be desirable to delay this alloying treatment by choice until the sintering stage, such as in the use of a pre-alloyed powder with poor pressing properties. The metal conferring the inferior properties to the alloy can be coated with a softer, more ductile metal thereby producing overall good pressing properties and reducing die wear. The ultimate association of the different metals in the mixture and the cold-work introduced during pressure promotes rapid diffusion on sintering and results in a compact with properties at least equal, if not superior to those which have been produced with a pre-alloyed powder.

The invention has the further advantage of replacing older methods of mixing metal powders, such as in double cone mixers, in twin shell mixers, in rod mills and in ball mills according to conventional practice. In many instances, cold-work produced during mixing is objectionable because the powders do not then deform easily during pressing, resulting in lower green densities and increased die wear. This is particularly the case with any form of milling operation. Other deleterious features of the latter form of mixing are, of course, possible contamination of the desired product from the grinding medium and/or the lining of the mill and the danger of oxidation. The cold-work and oxidation produced during milling by conventional methods often makes it necessary to re-anneal the powder and this added considerably to the cost of the raw material.

A further important advantage of the method of the present invention of producing composite metal powders is that a metal which would tend to oxidize easily in attrition or milling can be coated under reducing conditions with a more chemically stable metal to protect it from

	Composite Metal	Composition of Solution, Grams per litre		Composition of Product—Composite Metal Powder	Reduction Time, Minutes	Physical Characteristics
		In Solution	"Dispersed Metal"			
1	Fe+Ni+Co	Ni 23.6, Co 31.6	Fe 23.6	Fe:Ni:Co=30:30:40	30	Finely divided composite powder of about 9.6 microns.
2	Cr+Ni+Co	Ni 11.7, Co 23.6	Cr 23.6	Cr:Ni:Co=40:20:40	60	Finely divided composite powder about 12.6 microns.
3	(Mo+Fe)+Ni	Ni 33	Mo 14, Fe 3	Mo:Fe:Ni=28:6:66	10	Finely divided composite powder about 10.7 microns.
4	Cu+Ni	Ni 55.5	Cu 30	Cu:Ni=35:65	120	Finely divided copper nickel composite powder.
5	Cr+Ni	Ni 32	Cr 64	Cr:Ni=2:1	10	Finely divided composite powder.
6	Cr+TiC+Ni	Ni 51	TiC 7, Cr 14	Cr:TiC:Ni=20:10:70	10	Do.

It will be understood that these examples are for the purpose of illustrating the operation of the invention in the preparation of composite powders designed for use as conventional alloys, such as brass, bronze, Monel metal, iron-copper alloys, iron-nickel alloys, nickel-chromium alloys, cobalt-nickel alloys, iron-nickel-cobalt alloys and molybdenum-iron-nickel alloys.

The scope of the method is not limited, of course, to the production of these specific alloys. Rather, it can be employed with advantage in the production of composite powders which include one or more metals described as suitable for use as "dispersed metals" or nuclei and one or more of metals of different physical and/or chemical properties of the group of metals adapted to be precipitated as metal powder from an ammoniated solution by reaction with a reducing gas at elevated temperature and pressure.

The method of the present invention possesses a number of important advantages. It provides a method of pro- oxidation during subsequent processing. In certain instances, it may be desirable to arrange that the protective metal or a metal added to facilitate sintering can be removed during the sintering operation to leave a pure metal consisting only of the metal or metals of the nucleus.

What we claim as new and desire to protect by Letters Patent of the United States is:

1. The method of producing a composite metal powder comprised of at least two different metals which comprises dispersing solid particles of a metal in an ammoniated solution in which said particles are insoluble under reducing conditions and which contains, in solution, a compound of a metal selected from the group consisting of osmium, rhodium, ruthenium, iridium, gold, platinum, palladium, silver, copper, arsenic, tin, nickel and cobalt and having properties which are different from those of the dispersed metal particles, reacting the solution with a reducing gas at a temperature above about 200° F. and

under a positive partial pressure of reducing gas to precipitate from said solution particles of metal in elemental form on said dispersed metal particles, continuing the reducing reaction to coat said dispersed metal particles with said precipitated metal, and thereafter separating and recovering composite metal particles from the solution, said dispersed metal particles being present in said solution during the reducing reaction in amount sufficient to form, with said precipitated metal powder, a composite metal powder adapted to be compacted.

2. The method of producing a composite metal powder comprised of at least two different metals according to claim 1 in which solid particles of at least one metal selected from the group consisting of copper, silver, gold beryllium, zinc, cadmium, boron, aluminum, indium, titanium, germanium, zirconium, tin, hafnium, lead vanadium, niobium, antimony, tantalum, bismuth, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, ruthenium, rhodium, platinum, palladium, osmium, iridium, uranium and thorium are dispersed in the ammoniated solution subjected to the reducing reaction.

3. The method of producing a composite metal powder comprised of at least two different metals according to claim 1 in which the dissolved metal compound is a member of the group consisting of silver, copper, nickel and cobalt.

4. The method of producing a composite metal powder comprised of at least two different metals according to claim 1 in which the reducing reaction is continued to obtain composite metal particles which contain a predetermined ratio of dispersed metals to precipitated metal.

5. The method of producing a composite metal powder comprised of at least two different metals according to claim 1 in which a catalyst having a higher reducing potential under reducing conditions than the reducing gas employed is present in the solution subjected to reaction with the reducing gas.

6. The method of producing a composite metal powder comprised of at least two different metals according to claim 1 in which the dissolved metal compound is present in the ammoniated solution as a salt selected from the group consisting of sulphate and chloride.

7. The method of producing a composite metal powder comprised of at least two different metals according to claim 1 in which the dissolved metal compound is present in the ammoniated solution as a salt selected from the group consisting of sulphate and chloride and the reducing reaction is conducted at a temperature above about 200° F. and under a partial pressure of hydrogen above about 50 pounds per square inch.

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Patented May 5, 1959

1

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SINTERED Ni-Al-Zr COMPOSITIONS

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No Drawing. Application December 28, 1956
Serial No. 631,074
2 Claims. (Cl. 29—182)

This invention relates to an alloy composition having high temperature oxidation resistance and high temperature stress-to-rupture resistance, and, the process for making the same.

The composition of this invention is especially desirable for service at elevated temperatures and is particularly applicable for the manufacture of parts which are subjected to corrosive fluids especially where such parts are to be subjected to corroding conditions within a corroding atmosphere at high temperatures.

In the search for high-temperature materials for such application, numerous Ni-Al alloys have been tried, but without achieving satisfactory results. Among the principal literature references describing such Ni-Al alloys, are the articles of H. V. Kinsey and M. T. Stewart ("A Nickel-Aluminum-Molybdenum Creep Resistant Alloy," Canadian Journal of Research, vol. 27, sec. F, pp. 80–98; "Nickel-Aluminum-Molybdenum Alloys for Service at Elevated Temperatures," Transactions of the ASM, vol. 43 (1950) pp. 193–225), wherein they state that Ni-Al alloys containing a phase identified as NiAl, are unsuited for the manufacture of gas turbine blades. On page 197 of the ASM Transactions article, for example, they say, "The usefulness of the alloy disappears when the ratio of nickel to aluminum becomes 6:1 or less. This deterioration of properties coincides with the appearance of a phase (Fig. 15) identified as NiAl," and again, on page 225 of the same article, it is stated, "We have produced test bars consisting completely of NiAl. These bars would literally fall apart on handling, apparently from lack of cohesion between the grains."

Among the objects of the invention is a high-temperature material or shaped body combining as a principal ingredient a nickel-aluminum alloy or the intermetallic compound NiAl, but which does not deteriorate and which retains a high transverse rupture strength for a prolonged period at temperatures of about 1000° C. and higher.

The present invention is based on the discovery that by forming a shaped body by a powder metallurgy process out of particles of a composition containing essentially the intermetallic compound NiAl and an addition of 2% to 7% zirconium, the resulting body may be given by powder metallurgy techniques 100% density, and it will retain high corrosion resistance and the desired high transverse rupture strength not only at temperatures in the range up to 1000° C. but even at temperatures higher than 1000° C., such as 1100° C. to 1200° C. and even higher.

The foregoing and other objects of the invention will be best understood from the following description of exemplifications thereof.

The intermetallic compound NiAl consists of about 68.5% nickel and 31.5% aluminum, but small variations on both sides of the exact stoichiometrical proportion will not materially affect its properties, a larger variation being permissible on the side of excess nickel so that the most desirable range of proportions from the standpoint of oxidation resistance corresponds to an Ni/Al ratio varying from 65:35 [illegible]. Of the known NiAl compounds, the highest [illegible] resistance is exhibited by NiAl containing about 5% excess nickel.

2

According to the invention, shaped bodies of the same high corrosion resistance as the best prior NiAl materials, but having a higher order of transverse rupture strength at elevated temperatures, are obtained by forming the shaped bodies with powder metallurgy methods out of particles of Ni and Al generally corresponding to the NiAl compound, and containing in addition, 2% to 7% Zr, and treating the ingredients to homogenize them into an NiAl alloy containing in solid solution the Zr content. Particularly desirable bodies of great corrosion resistance at elevated temperatures and high transverse rupture strength in the range up to 1000° C. and higher, are obtained by forming them out of metal particles corresponding generally to the compound NiAl, with an addition of 3% to 6% Zr. In general, it is desirable that the Zr addition should be of high purity. Good results are obtained by adding the zirconium in the form of zirconium hydride. In practice, the powder particles for the shaped body are advantageously first produced out of a mixture of nickel powder, aluminum powder and zirconium hydride powder, which mixture is heated at an elevated temperature until an exothermic reaction starts, which further raises the temperature of the mixture to the temperature at which the ingredients of the mixture are formed into a porous, homogeneous, conglomerate containing Ni, Al and Zr in proportions corresponding to the ingredients of the mixture. The so-obtained porous conglomerate is reduced to a powder by crushing and milling to a fine particle size such as —325 mesh. The resulting fine NiAl+Zr powder is then formed into the desired shaped product by cold-pressing or compacting, presintering, followed by final sintering, or by cold-pressing followed by sintering, or by hot-pressing. The resulting fine NiAl+Zr may also be formed into shaped bodies by hydrostatic pressing or slip-casting, followed by presintering, final shaping and final sintering.

A feature of the invention is the fact that a compacted body of homogeneous powder particles of the formula generally corresponding to NiAl containing 2% to 7% Zr in solid solution is densified to 100% density and great high-temperature strength within a sintering time of only about five minutes. Compacted or cold-pressed NiAl+Zr powder particles may be given the desired 100% density by sintering at temperatures between 1500° C. and 1600° C. in vacuum or under a protective atmosphere of hydrogen or an inert gas such as argon for 2 to 5 minutes. When the NiAl+Zr powder particles are formed into shaped bodies by hot-pressing, the hot-pressed powder body is heated to about 1325° C.–1425° C. for about ninety seconds to give it 100% density.

The heating of the powder mixture of the nickel powder, aluminum powder and zirconium or zirconium hydride powder, is done in an enclosure or crucible of a material which does not react with the ingredients of the metal powder mixture when they undergo an exothermic reaction in forming the zirconium-containing NiAl. Good results are obtained by using as a crucible enclosure for the powder mixture of Ni, Al and Zr particles, a crucible or enclosure of magnesia. It is good practice to place around the magnesia crucible enclosure containing the powder mixture of Ni, Al and Zr, an outer enclosure of graphite.

Before treating to the temperature of the exothermic reaction, it is good practice to compact the powder mixture of Ni, Al and Zr into solid slugs of a size convenient for charging the crucible enclosure. In practice, good results are obtained by compacting the powder mixture of Ni, Al and zirconium hydride particles into slugs about two inches in diameter and two inches high, having a density of about 3 gm./cc. (gram/cubic centimeters).

The shape, size and density of the compacted powder shapes are not important as long as the metal powder mixture is retained in the form of solid pieces suitable for ready charging into the interior of the crucible enclosure in which they are subjected to the exothermic reaction. To prevent binding, the walls of the compacting die and compacting punches are suitably lubricated, for instance with a camphor-ether solution.

The crucible enclosure in which the powder particles of Ni, Al and Zr are heated for bringing about the exothermic reaction and homogenization of the ingredients, is provided with an inlet duct and an outlet duct for admitting hydrogen to the interior of the crucible into contact with the treated powder mixture and for discharging the hydrogen from the interior of the heated crucible enclosure. It is of advantage to use purified dry hydrogen. This can be done by any conventional procedure, for instance, by passing the hydrogen through a palladium catalyst followed by passing it through a desiccant tower, for instance one containing activated alumina. It is good practice to purge the system with pure hydrogen before raising the temperature of the contents from normal temperature to the reacting temperature.

The heating of the Ni, Al and zirconium hydride powder mixture to the reaction temperature may be effected by high-frequency induction heating, for instance, by surrounding the crucible enclosure with its powder mixture content with a water-cooled copper coil through which high-frequency electric current is fed, for heating the crucible contents by induced electric currents. The hydrogen in the interior of the crucible is ignited as the metal powder charge is heated by the induced currents. Depending on the amount of the metal powder charge, a longer or shorter time is required for bringing the powder mixture charge of the crucible to the reaction temperature between 800° C. and 1200° C. The exothermic reaction raises the temperature of the heated powder mixture to a higher temperature, such as 1650° C. Purified hydrogen is continuously passed through the interior of the heated crucible as the charge is being heated to start the exothermic reaction, and the passing of the hydrogen is continued until the reaction is completed and the ingredients of the powder mixture charge are homogenized into NiAl containing the small addition of zirconium in solid solution therewith. As an example, a powder charge of Ni, Al and Zr, in the above-specified proportions, filling a cylindrical crucible interior 4 inches inside diameter and 17 inches high, treated in the manner described above, will be heated by induction to the exothermic reaction temperature within about 20 minutes, and a homogeneous conglomerate of the reaction product is obtained by continuing the treatment for about 90 minutes at an elevated temperature of 1200° C. under an atmosphere of pure hydrogen. The purified hydrogen is passed continuously through the interior of the crucible until after the completion of the exothermic reaction and the homogenizing of the contents of the reacted powder mixture, the temperature of the reaction product is lowered to normal temperature. The combined exothermic and homogenizing treatment carried on at the elevated temperature yields a porous but tough conglomerate containing NiAl with the small addition of zirconium in solid solution therewith. The so-obtained conglomerate is removed from the crucible and blasted with grit or sand to remove any surface contaminants. The conglomerate is then crushed into a powder, such as −100 mesh particle size, and the powder body is further reduced in size, as by ball-milling in a tungsten carbide mill under a cover of a suitable protective liquid such as ethyl alcohol, until the particles of the conglomerate have been reduced to a size of 2 to 5 microns, or −325 mesh particle size. After the treated conglomerate has thus been reduced to the fine particle size, the powder particles are suitably separated from the cover liquid, such as ethyl alcohol, as by filtering and drying.

Out of the so-obtained powder mixture of fine, homogenized particles of NiAl containing Zr in solid solution, shaped bodies may be produced either by cold-pressing or compacting, followed by sintering; or cold-pressing followed by presintering at a relatively low temperature, followed by a final shaping or coining, followed by a short final sintering at a higher temperature; or by hot-pressing the powder mixture. Good results are obtained by cold-pressing or compacting the powder mixture with 15,000 to 20,000 p.s.i. (pounds per square inch). It is of advantage to use a small amount of lubricant addition with the metal powder mixture when it is so compacted. Any of the known liquid lubricants used in similar compacting processes may be used. Good results are obtained by adding 2% camphor dissolved in ether, to the homogenized metal powder mixture under a fume hood, and the powder body should be compacted relatively soon after admixture of the lubricant, for instance within a day therefrom. It is of advantage to apply a lubricant to the surfaces of the compacting dies and punches, for instance by applying thereto a coating of a similar ether-camphor solution.

Such compacted green body of zirconium-containing NiAl does not have sufficient strength for machining into the final accurate shape. If machining or final shaping is to be done, the compacted zirconium-containing NiAl powder body is subjected to presintering. Good results are obtained by presintering at a temperature of between 1000° C. and 1100° C. for about 10 to 20 minutes under vacuum, followed by cooling to about 150° C. before the vacuum is broken. The so presintered body may be readily machined or coined to give it the final desired shape. Instead of presintering under vacuum, the presintering operation may be carried on under an atmosphere of purified dry hydrogen.

The so-compacted and presintered and finally shaped body is then subjected to final sintering. The final sintering may be done under vacuum or in an atmosphere of purified dry hydrogen at a temperature of between 1500° C. and 1600° C. Final sintering for 2 to 5 minutes at temperatures between 1500° C. and 1600° C. results in complete densification of the compact to full or 100% density. Since the final sintering and densification results in an inner shrinkage of about 20%, the compacting dies in which the shaped bodies are formed are dimensioned to give over-sized compacts which after the presintering, machining or coining, and final sintering to full densification and shrinkage, yield a shaped body of the desired final dimensions.

Instead of presintering followed by coining or machining, followed by final sintering, the desired shaped bodies may be produced by subjecting the over-sized compacted zirconium-containing NiAl bodies to a single sintering operation at between 1500° C. and 1600° C. in vacuum or under pure hydrogen for about 3 to 5 minutes up to 10 minutes, whereby the compact is sintered to full density and full strength.

Hydrostatic pressing may be used for forming a zirconium-containing NiAl powder body into the desired compacted shape. For instance, in forming such compact by hydrostatic pressure, the following procedure may be used: A powder body of zirconium-containing NiAl is placed in a rubber mold of desired shape the walls of which will yield when placed in a vessel containing a liquid pressure body which is subjected to pressure. The liquid pressure body may, for instance, consist of glycerin. The metal powder body has admixed thereto, a small amount of a binder such as 2% camphor dissolved in ether. The rubber mold filled with the metal powder body is sealed off and is placed in the pressure liquid, the pressure of which is increased, as by a hydraulic press, for instance, to ¼ to 4 t.s.i. (tons per square inch). Such hydrostatically pressed metal powder bodies may be presintered and further machined before final sintering, or subjected directly to

a final sintering operation, in the same way as described in connection with shaped bodies formed with a compacting die.

Zirconium-containing NiAl powder bodies may also be formed in the desired shape by slip-casting. To this end, the metal powder bodies have admixed thereto a suitable liquid such as water containing a polyvinyl alcohol resin for forming a thick metal powder slurry. The metal powder slurry is then poured into a plaster mold which is vibrated while the slurry is poured into it. After the slurry contents of the plaster mold have been dried by driving off the liquid, the shaped cast body is removed from the plaster mold and treated in the same way as the compacted metal powder bodies formed in metal dies.

The examples given below give additional details of procedures suitable for producing shaped bodies of NiAl containing in solid solution 2% to 7% Zr.

Example 1

Nickel powder of high purity, such as electrolytic nickel powder of 99.25% purity, having a particle size −100, +200 mesh, is mixed with aluminum powder of 99.5% purity, −30 mesh particle size, and with zirconium hydride powder, −100 mesh particle size, in proportions corresponding to a composition containing about 65.8% nickel, 30.2% aluminum, and 4% zirconium. The powder mixture is mixed by tumbling for 15 to 20 minutes, and compressed into slugs approximately 2 inches in diameter, one inch long. The slugs are placed in a crucible of magnesia which is enclosed by a magnesia closure cover, the covered magnesia crucible being in turn enclosed in a graphite enclosure. Purified dry hydrogen is passed through the interior of the crucible enclosure. The crucible enclosure and the powder content are heated by high-frequency induction currents, until an exothermic reaction takes place at about 1180° C. Purified dry hydrogen is passed through the interior of the crucible enclosure throughout the period during which the contents of the crucible enclosure are heated above normal temperatures and until they are cooled to normal temperatures. Thereupon the reaction conglomerate is removed from the crucible. The reaction conglomerate is porous and is reduced to powder by first crushing it, followed by milling, as in a tungsten carbide ball mill, to form out of the reaction conglomerate, powder particles of −325 mesh particle size. The ball-milling is done under ethyl alcohol, and the resultant NiAl+Zr powder is separated from the ethyl alcohol by filtering and drying under vacuum.

X-ray diffraction patterns of so-obtained powder show essentially the presence of NiAl with a greatly expanded lattice indicating that the zirconium content is taken into the NiAl lattice. A chemical analysis shows that the powder particles contain Ni, Al and Zr in proportions corresponding to the ingredients of the initial powder mixture.

A body of such zirconium-containing NiAl powder was mixed with 2% camphor dissolved in ether as a lubricant, and compacted in a die with a pressure of 17,000 p.s.i. The compact was subjected to sintering in an atmosphere of purified hydrogen at between 1530° C. and 1540° C. for 5 minutes, yielding a body having a density of 5.85 gm./cc. (grams over cubic centimeters), this being full 100% density. When subjected to transverse rupture tests, this material had a transverse rupture strength of 138,000 p.s.i. over a temperature range from zero up to 1000° C., and its transverse rupture strength increased above this value as the temperature was increased above 1000° C. Thus, at 1100° C. the transverse rupture strength of the material was 145,000 p.s.i. In contrast, the best prior similarly produced NiAl material exhibiting similar high corrosion resistance and consisting of NiAl plus an excess of 5% Ni in solid solution, although exhibiting a similar high transverse rupture strength at room temperatures, dropped rapidly in strength from 95,000 p.s.i. at 800° C. to 67,000 p.s.i. at 1000° C., and to 50,000 p.s.i. at 1100° C. Likewise in contrast, similarly produced NiAl material containing instead of 4% zirconium, 4% titanium, although exhibiting substantially the same transverse rupture strength up to 1000° C., rapidly lost its strength at above 1000° C., its transverse rupture strength dropping from 140,000 p.s.i. at 1000° C. to 80,000 p.s.i. at 1100° C.

Example 2

A sintered body of zirconium-containing NiAl was produced in the same way as in Example 1, except that the powder mixture out of which the homogeneous conglomerate was formed, consisted of a mixture of powder particles of Ni, Al and ZrH_2, corresponding to a composition consisting of NiAl containing 5% of excess nickel beyond the amount corresponding to NiAl, and 4% zirconium. A homogeneous powder mixture produced by the exothermic reaction treatment as described in connection with Example 1, when compacted and sintered as therein described, yielded a body of 100% density within five minutes of the sintering operation. The resulting sintered body had substantially the same transverse rupture characteristics as the body of Example 1.

Example 3

A sintered body prepared as in Example 1 was formed of an initial powder mixture of Ni, Al, and Zr, corresponding to a composition consisting of NiAl and 2% zirconium. A homogeneous powder mixture produced by the exothermic reaction treatment as described in connection with Example 1, when compacted and sintered as therein described, yielded a body of 100% density within 5 minutes of the sintering operation. The resulting sintered body had substantially the same transverse rupture characteristics as the body of Example 1.

An outstanding feature of shaped bodies of the invention, is the fact that in addition to exhibiting high corrosion resistance and high transverse rupture strength at temperatures above 1000° C., they also have a higher order of impact strength than other known NiAl bodies, a factor of critical importance in the practical application of such shaped bodies.

It will be apparent to those skilled in the art that the novel principles of the invention disclosed herein in connection with specific exemplifications thereof, will suggest various other modifications and applications of the same. It is accordingly desired that the present invention shall not be limited to the specific exemplifications shown or described therein.

I claim:

1. A shaped corrosion-resistant body having an extended surface which in operation is exposed to corroding fluids and great strains, said body consisting of sintered powder particles containing about 93% to 98% of a nickel-aluminum alloy of the approximate composition of the NiAl and an addition consisting of 2% to 7% zirconium in solid solution with said alloy, said nickel-aluminum alloy consisting of 65% to 75% nickel, the balance aluminum.

2. A shaped corrosion-resistant body having an extended surface which in operation is exposed to corroding fluids and great strains, said body consisting of sintered powder particles containing about 95% to 97% of a nickel-aluminum alloy of the approximate composition NiAl and an addition consisting of 3% to 5% zirconium in solid solution with said alloy.

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Patented Sept. 15, 1959

2,904,449

METHOD AND COMPOSITIONS FOR FLAME SPRAYING

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No Drawing. Application July 26, 1955
Serial No. 524,598

8 Claims. (Cl. 117—46)

The present invention is directed to methods of and compositions for applying refractory coatings onto a variety of surfaces. The invention finds particular utility in coating metal surfaces to protect the same against oxidation and other high temperature effects, but is also applicable to the coating of various surfaces such as glass, carbon, concrete, refractories, and various other materials.

The process of the present invention involves flame spraying a particulated material onto a surface under conditions such that the coating which results is securely bonded to the surface to be coated and, in most instances, provides a refractory thin outer shell making the coating useful in environments where it could not heretofore have been used in the absence of the coating. For example, the process of the invention finds particular application in the coating of metal surfaces for use in rocket nozzles, as coatings for turbine blading, and various other applications where a metal surface must be modified in order to adapt it for extreme high temperature conditions.

While the technique of flame spraying has been applied previously to metals and in some instances to ceramic materials such as refractory oxides, the latter have not always proven successful for various reasons. In many instances, attempts to coat surfaces with ceramic materials involved the deposition of a glassy coatings on the surface, resulting in the production of an amorphous coating. These coatings have generally been unsatisfactory for high temperature work because the glass and the underlying substrate have coefficients of thermal expansion which are immutable and seldom equal. As a consequence, the interface between them is usually stressed by heating or by cooling. Because of the brittle nature of glass, these stresses frequently cause failure in the coating by cracking or chipping. Accordingly, the present invention makes use of materials which are refractory but not glassy, i.e., they retain the crystalline structure of the starting materials without forming an amorphous glass composition during or after deposition of the coating onto the surface by the flame spraying process.

The improved results obtained by the process of the present invention are believed due, at least in part, to the recognition that the coating which is applied by the flame spraying process should retain its crystalline characteristics and should be a sintered rather than a completely fused coating. The results obtained from products produced according to the present invention have more than justified this assumption.

Accordingly, an object of the present invention is to provide an improved process for flame spraying various refractory materials onto surfaces.

Still another object of the invention is to provide an improved method for applying a sintered refractory coating onto a metal surface under conditions such that there is a good mechanical as well as possibly a chemical bond between the material of the coating and the underlying metal.

Another object of the invention is to provide an improved process for applying flame sprayed coatings which results in better distribution of the coating on the surface, and a more efficient use of heat.

Still another object of the invention is to provide improved compositions for use as flame spraying compositions.

In any flame spraying process, there are only a few variables which are under some degree of control by the operator. The first of these is the composition employed which, of course, is variable at will. The second is the size of the particles employed. A third is the flame temperature involved, which depends primarily upon the fuel being burned in the flame spraying torch. A fourth is the control of the residence time of the particles in the flame prior to the time the particles strike the surface. This, however, is not capable of wide variation because the particles must have a minimum velocity of a relatively high order in order to be propelled properly through the flame. Generally, the residence time of particles in the flame is measured in units of hundredths of a second, this being the interval between the time a given particle is injected into the flame and the time it appears as part of the coating on the object.

Basically then, the operator has control over the compositions, the size of the particles, and the flame temperature. Nevertheless, it frequently happens that the sintering temperature of the particular material chosen for its refractory properties is in excess of the temperature which the particles reach during their presence in the flame. In these situations, new techniques are required to achieve the desired sintering effects and the retention of the desired crystalline structure.

Perhaps the simplest technique for increasing the temperature of the particles is to reduce the particle size as low as possible. However, except in very few cases, the reduction of particle size is, in and of itself, insufficient to create the difference between a sintering and a non-sintering condition in the flame. In addition to this, there is the additional complication that the reduction of the particles to extremely small sizes presents feeding problems in delivering the particles into the flame.

A more satisfactory solution resides in providing fluxes in combination with the refractory oxides which form a liquid medium in which the sintering reaction may occur. Particularly good results have been obtained by employing phosphate binders, particularly the metaphosphates and pyrophosphates of calcium and magnesium in conjunction with alpha alumina. Generally from about 2% to about 10% of the composition by weight may consist of the phosphate, the remainder being the refractory oxide. The relatively non-volatile calcium and magnesium phosphates are preferred, but the more volatile sodium and potassium phosphates may be employed in addition to the preferred compounds.

One particularly effective means for raising the temperature of the flame so that is provides a sintering atmosphere for the particles contained therein is to include a flame catalyst in the composition fed into the flame. A flame catalyst is a material which is capable of catalyzing the oxidation reaction being carried out in the flame and thereby raise the temperature of the catalyst surface. In the case of an oxyhydrogen torch, for example, one would select a catalyst material which is

capable of catalyzing the oxidization of hydrogen. Whether or not a given material is a flame catalyst is a relatively easy thing to determine. However, the theory of flame catalysis has never been extensively developed. The following theoretical explanation has been developed as a result of the experimental work leading up to the present invention, and seems to be borne out by the results obtained.

It appears that a metal oxide, to catalyze the reaction in the flame must have the following characteristics. First of all, the catalyst should be a metal oxide in which the oxygen to oxygen distance on the outside of the solid oxide is close to that of a closed packing system, whether of the cubic or the hexagonal type. In other words, the interatomic distance should be close to the value of 2.92 Angstrom units characteristic of the close packing system. When this condition exists, it seems to favor the formation of hydroxyl ions on the surface of the catalyst, thereby, tending to carry the combustion reaction toward completion, since the formation of hydroxyl ions is believed to be an intermediate step in all of the gas combustion reactions which produce water as an end product.

The next requirement is that the catalyst be partially reduced by the fuel gas used. For example, the oxides of most of the transition metals are reduced by hydrogen at the temperature of the oxyhydrogen flame.

The flame catalyst used need not be an oxide; if a metal which will coordinate oxygen ions or hydroxyl groups is used. This metal will also act as a flame catalyst. Thus nickel oxide is not a particularly good flame catalyst because it is only slightly reduced by hydrogen, while finely powdered nickel metal, which oxidizes slightly in the neutral oxyhydrogen flame, is more effective. Where the catalyst oxide is volatile (molybdenum or vanadium oxides for example) the heat gained by flame catalysis may be lost as heat of vaporization, but if the particles are rendered sufficiently incandescent before vaporizing, their radiation serves to heat adjacent non-catalytic particles. In summary those materials may be regarded as effective additives which by their presence increase the apparent optical temperature of the incandescent powder stream. A list of such additives includes magnesium pyrophosphate, sodium acid phosphate, ilmenite (a ferric titanate mineral) aluminum acetate, aluminum phosphate, chromium metal or reduced chromium oxide, and lithium aluminate; all of these may be combined with alpha alumina as the major constituent of the powder feed.

Generally, I prefer to include about 2 to 8% of the flame catalyst in the composition, but actually the percentage of the flame catalyst may vary from very minute amounts such as 0.1% to as high as 10% or more.

Certain flame catalysts work better with selected refractory materials. For example, cerium oxide provides an excellent flame catalyst with zirconia but is not particularly effective with other types of refractories. Vanadium oxide is very effective with alpha alumina. Cobalt oxide is particularly effective with zirconia in an oxyacetylene flame, while gamma alumina is a flame catalyst for oxyhydrogen reactions. Similarly, chromic oxide is a very effective flame catalyst with zirconia while manganese dioxide is effective with alpha alumina.

The addition of a flame catalyst is particularly effective in conjunction with the application of alpha alumina as a flame sprayed coating. It has been demonstrated that the addition of even a small amount of the flame catalyst can make the difference between securing an adherent, sintered coating of the alumina onto the surface of the article or a coating which is very likely to crumble off or flake off.

The preferred vanadium oxide may be added to the flame as such, but it is preferable to add a material to the flame which will decompose under the conditions of the flame to yield either the vanadium trioxide or the vanadium pentoxide. Hence, the starting material is preferably a compound such as ammonium vanadate.

In connection with the flame catalysis, it should be noted that the theoretical temperature of an oxyacetylene flame is about 3000° C., and that the actual flame temperature is on the order of 2200° C. In the case of the oxyhydrogen torch, the theoretical temperature and the actual temperature are about 300° C. lower than those of oxyacetylene. The sintering temperature of alumina is on the order of 1200° C.

While the flame temperature varies substantially, depending upon the type of fuel being burned, it is preferable to employ a flame which has a temperature of at least 1500° C. in order to insure adequate sintering of the refractory oxides. It is also desirable to employ a "soft" flame, that is, a flame having little or no excess oxygen over the amount stoichiometrically required for the combustion reaction to go to completion. In fact, the flame may be a reducing flame and still operate satisfactorily.

The increase in flame temperature which occurs through the use of flame catalysts also has the desirable effect of helping to break up the particles in the flame, thereby producing still smaller particle sizes which, in turn, again helps to increase the effective temperature of the particles.

It is interesting to note that the compound gamma alumina is an auto-catalyst for an oxhydrogen flame, so that the temperature of the flame is automatically increased by the injection of the gamma alumina powder into the flame. Accordingly, this compound alone is a very suitable starting material for the application of alumina coatings. The expensive gamma alumina may be replaced wholly or in part by using a material which forms gamma alumina in the flame, e.g. alpha alumina monohydrate, aluminum acetate, or bauxite. The absorption of heat by the powder can be accelerated by inclusion of an isomorph of gamma alumina which either acts as a flame catalyst (cobalt oxide) or to increase, in solid solution, its absorption of radiant heat (titania), or as a flux (magnesium fluoride).

Instead of modifying the flame temperature, or in addition thereto, adequate sintering can be achieved by combining two compounds which are isomorphous in structure so that they are capable of forming a fluid phase for a short time under the influence of the flame to rearrange themselves into a crystalline material having a higher melting temperature than other combinations of the components. The most important class of compounds which can be produced in this way are the compounds having a spinel structure. True spinel is the combination of magnesia and alumina in a face-centered cubic lattice, and this type of compound can be produced in the process of the invention by injecting suitable amounts of alumina and a source of magnesium atoms into the flame. The resulting coating is found to contain not only spinel itself ($MgO.Al_2O_3$) but gamma alumina, which has the spinel structure and nearly the same lattice parameters, and is therefore said to be isomorphous with spinel and to a certain extent capable of forming solid solutions with it. For this reason particularly good results are obtained when the refractory material is itself a spinel or perovskite, since the latter are close-packed oxygen lattices and therefore flame catalysts. As examples of the spinels, gamma-alumina, chromite ($FeCr_2O_4$), magnetite (Fe_3O_4), picrochromite ($MgO.Cr_2O_3$), reduced ilmenite

($Fe_2TiO_4.Fe_2O_3$)

nickel aluminate, ($NiAl_2O_4$), and magnesium titanate, (Mg_2TiO_4). The cell size for such spinels varies from 7.9 for gamma-alumina up to 8.48 for the ferrite spinels; the latter are consequently more nearly isomorphic with zirconia rather than with alumina systems. It is interesting to note that lithium aluminate forms, with moderate heating, a spinel ($LiAl_5O_8$) in which the so called "de-

fect gamma" structure is stabilized. As examples of perovskite ($CaTiO_3$) structures, the major types which have been investigated fall into the ilmenite ($FeTiO_3$) and corundum (alpha-alumina) systems, in which the metal atoms occupy two-thirds of the octahedral holes in a hexagonal close-packed oxygen lattice. The pyrophosphate structure can be regarded as an infinite three-dimensional structure of PO_4 tetrahedra linked in hexagonal close packing by magnesium ions above and below the hexagon centers.

Particularly good results are obtained if the alumina employed is a gamma alumina or a source thereof such as aluminum acetate. In this connection, it should be noted that while the present disclosure deals primarily with the use of refractory oxides as the coating materials, it will be evident that the oxide per se need not be employed, but compounds which yield the oxides under the conditions of the flame are also usable, and in some cases preferable. For example, carbonates of magnesium, aluminum, or zirconium can be employed as starting materials or as mentioned previously, aluminum acetate is an excellent source of gamma alumina. The use of aluminum acetate has the further advantage of providing an anti-clogging agent in the composition to prevent caking or packing of the alumina particles present.

A source of vanadium oxide in the flame provides uniquely improved results because vanadium oxide is isomorphous with alumina and is also a flame catalyst, as previously mentioned.

The applied coating need not consist entirely of the spinel or the perovskite type structure, as the spinel or perovskite serves as an effective binder for systems composed predominately of magnesia, alumina or the like even when present in relatively small amounts.

Still another technique which is effective to raise the temperature of the particles in the flame is that of adding a material to the composition which will undergo an exothermic reaction while in the flame. Specifically, certain metals can be added in finely divided form to the oxides or sources of oxides injected into the flame and such metals will undergo an oxidation which effectively raises the temperature of the particles in the flame. Particularly preferred for this use is aluminum powder which becomes oxidized under the conditions of the flame to produce aluminum oxide and serves as an added source of alumina in the coating. In addition, metals such as chromium, nickel, cobalt and silicon can be employed for the same purpose. Preferably, about 5 to 7% by weight of the composition may consist of the powdered metal through as little as 1/10 of 1% or as high as 10% may be used in some cases. It is not necessary to use a pure metal, as long as the material used represents a source of the metal in the flame. Thus, ferrosilicon is a good source of silicon, and ferromanganese is a good source of manganese.

The equipment used to apply the flame sprayed coating may be any of a variety of flame spraying apparatus. The simplest consists of an oxyacetylene or oxyhydrogen cutting torch or blowpipe which is modified by the inclusion of a venturi nozzle to permit injection of the finely divided particulated mixture of the refractory oxide or the like together with any other additive such as a flame catalyst, powdered metal, or the like. The powdered mixture is carried into the flame in the oxygen stream and the other gaseous stream such as hydrogen, methane, acetylene, or the like is injected separately into the venturi.

As previously indicated, the particle size being fed into the flame may vary substantially. Particles as low as 2 or 3 microns in maximum dimension have been used successfully, and particles as large as 30 mesh have also been employed satisfactorily. However, for most purposes, a particle size between about 200 mesh to less than 500 mesh will be found to be the most satisfactory.

In order to improve the characteristics of the bond which occurs between the coating and the underlying surface, it is desirable to roughen the surface prior to application of the coating. This can be done in the case of a metal for example by phosphatizing the surface or by abrading it as by sand blasting or the like.

One of the advantages of the coatings of the present invention is that they are considerably more efficient in the utilization of the heat of the flame than other types of flame spraying systems. Since the particles are in discrete form, they need only be surface heated to the extent of having the particles bond together by sintering action rather than utilize a considerable amount of the heat of the flame in melting a solid rod of the material and spraying it as a molten mass onto the surface to be covered. In operating the process of the present invention, the particles should reach the surface to be coated at their highest temperature. This means that for every application, there is probably a limited range of spacing which can be employed between the nozzle and the surface being coated. This spacing is easily determined because at the proper spacing, the coating goes on fastest, and the position at which the coating is being applied at the fastest rate is readily visible to the eye.

One of the other outstanding advantages of the process of the present invention resides in the fact that the article to be coated need not be heated prior to application of the coating. This means that the system of the present invention can produce prestressed coatings on metal bodies.

For example, stainless steel has a coefficient of thermal expansion which is substantially lower than that of alumina. However, the alumina when applied is quite hot, while the steel is cold so that when upon cooling, the coating is put in compression about the stainless steel body. As a consequence, upon sudden heating, further compressive stress in the coating occurs, but the di-oriented and somewhat porous nature of the coating resists the tendency toward failure by chipping which occurs in vitreous coatings under compression on cooling, the compressive stress in the coating is reduced but is not made destructively negative even when the sample is plunged at red heat into water. As a result, these coatings are less dependent upon a close watch of thermal expansion coefficients than are vitreous coatings, and are at the same time less rigid or brittle.

The following examples illustrate the method of applying the coatings to the present invention, and the results obtained.

Example I

A flame spraying mixture was prepared by mixing 200 parts by weight of 60 mesh alumina (corundum) with 20 parts by weight of magnesium pyrophosphate, and 5 parts by weight of aluminum acetate. The powder was injected into an oxygen stream being fed to an oxyacetylene torch. The tip of the torch was held a few inches away from a steel plate which was to be coated. The flame sprayed coating which resulted built up an excellent film and was tightly adherent to the surface. Improved results were obtained when the surface of the steel was pretreated with a solution of phosphoric acid and sand blasted prior to application of the flame sprayed coating.

Example II

A flame-spraying mixture was prepared by grinding mullite ($3Al_2O_3.2SiO_2$) to −500 mesh. (A small amount, 0.1%–1.0%, of aluminum acetate may be added to reduce packing of the powder in the feed hopper.) The powder was aspirated into the oxygen stream of a hand blowpipe (National Type 3A or equivalent modified to give unrestricted oxygen flow) and oxygen and hydrogen pressures were balanced to give a neutral or slightly reducing flame about 7 inches long. A steel plate, lightly sand-blasted, was coated most rapidly when the flame was directed normal to the metal surface and about 5 inches

therefrom. Using a No. 3 tip for fine spraying (into crevices, etc.) and a No. 5 tip for relatively flat or large areas, a rate of coating buildup of from ½ to 1 mil per square inch per minute was attained. The coating was very refractory and tightly adherent to the metal surface.

Example III

A flame spraying mixture was prepared using ground acid-washed corundum (− 325 mesh) with 5 percent of lithium aluminate added. The powder was fed into the apparatus described in Example II. The rate of spray application (for Ox-5 tip, hydrogen pressure 10 p.s.i.g., oxygen pressure 16 p.s.i.g.) was found to be approximately 2 mils per square inch per second. This was a weight deposition rate of approximately 3.3 gm./second. Optical particle temperature in the flame was in excess of 1150° C. The white coating had a superficial vitreous appearance, tristimulus reflectivities of 75.6, 76.0, and 71.6 in the green, amber, and blue ranges, and an average density approaching 3.0 gm./cc., or a porosity of 15–18 percent. Its Knoop hardness was 1313. The Vickers hardness values depended somewhat on the thickness of coating and hardness of underlying metal but were generally in the range 1580–1640.

The coating was successfully applied to glass, a variety of refractories, steel and ferrous alloys, electrode carbon, titanium, magnesium, molybdenum, aluminum, gold, platinum, palladium, nickel and chromium plate, Inconel, Nichrome, Kanthal A, and Duriron. Although the coating is difficult to apply to copper and its alloys, good adhesion has been obtained in a number of instances. When non-washed corundum is used, the coating is not white but adheres equally well. The composition of the coating, estimated from X-ray diffraction photographs, is less than one-half alpha-alumina and more than one-half gamma alumina.

This coating is quite refractory, possesses a high degree of electrical resistivity, and may be built up in thickness, coatings approaching 0.1 inch thick having been obtained.

If a small percentage of finely powdered nickel is milled into the coating composition, a coating is obtained which contains alpha alumina, gamma alumina, and a spinel structure believed to be $NiO.Al_2O_3$ which is apparently isomorphous with gamma alumina. This coating is highly resistant to attack by mineral acids. The inclusion of fine aluminum powder in the mixture produces a coating with a high degree of resistance to oxidation of the underlying substrate.

Example IV

Certain mineral products can, if ground sufficiently fine, be fed directly into the flame without additives. These include ilmenite, rutile, kyanite, sillimanite, bauxite, and zircon. Mesh sizes should be less than 325 (44 microns) and results are more consistent if the powders are less than 500 mesh (30 microns) in size.

All of these minerals contain iron as a natural impurity homogeneously dispersed in the crystalline structure of the mineral.

For such minerals, any addition which increases the flame temperature improves the maximum permissible spraying rate or coating hardness. For example, fine aluminum powder, powdered ferrosilicon (50–90% Si), nickel, or chromium can be added to the coating composition. Powdered iron exerts a small but measurable improvement with ilmenite, but the resulting coating is not corrosion-resistant. Lithium aluminate, lithium fluoride, and powdered molybdenum increase the particle temperature slightly (50 to 100° C.). These coatings appear to be useful in applications where economy is paramount, as in forming skid-resistant coatings for metal gratings, refractory coatings for brick and the like.

I claim as my invention:

1. The method of applying an adherent refractory coating onto a surface, which comprises injecting solid crystalline particles of an oxygen-containing material which material is refractory at 1200° C. into a gaseous stream being fed into a continuous flame generating device, maintaining the flame temperature and residence time of said particles in said flame at a value to heat the particles to sintering temperature in the flame, and impinging the hot particles on the surface to form a crystalline deposit of the resulting sintered particles as an adherent coating on said surface.

2. The method of applying an adherent refractory coating onto a surface, which comprises injecting a mixture of solid particles of crystalline isomorphous oxygen-containing materials which materials are refractory at 1200° C. into a gaseous stream being fed into a continuous flame generating device, maintaining the flame temperature and residence time of said particles in said flame at a value to heat the particles to sintering temperature in the flame, and impinging the hot particles on the surface to form a crystalline deposit of the resulting sintered particles as an adherent coating on said surface.

3. The method of applying an adherent refractory coating onto a surface, which comprises injecting a mixture of particles of alpha alumina and lithium aluminate into a continuous flame of a combustion zone, maintaining the flame temperature and residence time of said particles in said flame at a value to heat the particles to sintering temperature in the flame, and impinging the hot particles on the surface to form a crystalline deposit of the resulting sintered particles as an adherent coating on said surface.

4. The method of applying an adherent refractory coating onto a surface, which comprises injecting into a continuous flame of a combustion zone a mixture of particles of a solid crystalline oxygen-containing material which material is refractory at 1200° C. and from about 0.1% to about 10% by weight thereof of a powdered metal, maintaining the flame temperature and residence time of said particles in said flame at a value to heat the particles to sintering temperature in the flame, and impinging the hot particles on the surface to form a crystalline deposit of the resulting sintered particles as an adherent coating on said surface.

5. The method of applying an adherent refractory coating onto a surface, which comprises injecting into a continuous flame of a combustion zone a mixture of particles of a solid crystalline oxygen-containing material which material is refractory at 1200° C. and from about 0.1% to about 10% by weight thereof of a powdered oxide catalyst for the combustion reaction, maintaining the flame temperature and residence time of said particles in said flame at a value to heat the particles to sintering temperature in the flame, and impinging the hot particles on the surface to form a crystalline deposit of the resulting sintered particles as an adherent coating on said surface.

6. The method claimed in claim 1 wherein said oxygen-containing material is selected from the group consisting of alpha alumina and zirconia.

7. The method of applying an adherent refractory coating onto a surface, which comprises injecting particles of ilmenite into a continuous flame of a combustion zone, maintaining the flame temperature and residence time of said particles in said flame at a value to heat the particles to sintering temperature in the flame, and impinging the hot particles on the surface to form a crystalline deposit of the resulting sintered particles as an adherent coating on said surface.

8. The method of applying an adherent refractory coating onto a surface, which comprises injecting rutile particles into a continuous flame of a combustion zone, maintaining the flame temperature and residence time of said particles in said flame at a value to heat the particles to sintering temperature in the flame, and impinging the hot particles on the surface to form a crys-

talline deposit of the resulting sintered particles as an adherent coating on said surface.

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E 852

Oct. 13, 1959 G. GUTZEIT ET AL 2,908,589

METHOD OF FLAME SPRAYING AN ALLOY AND THE RESULTING ARTICLE

Filed April 16, 1957

FIG 1

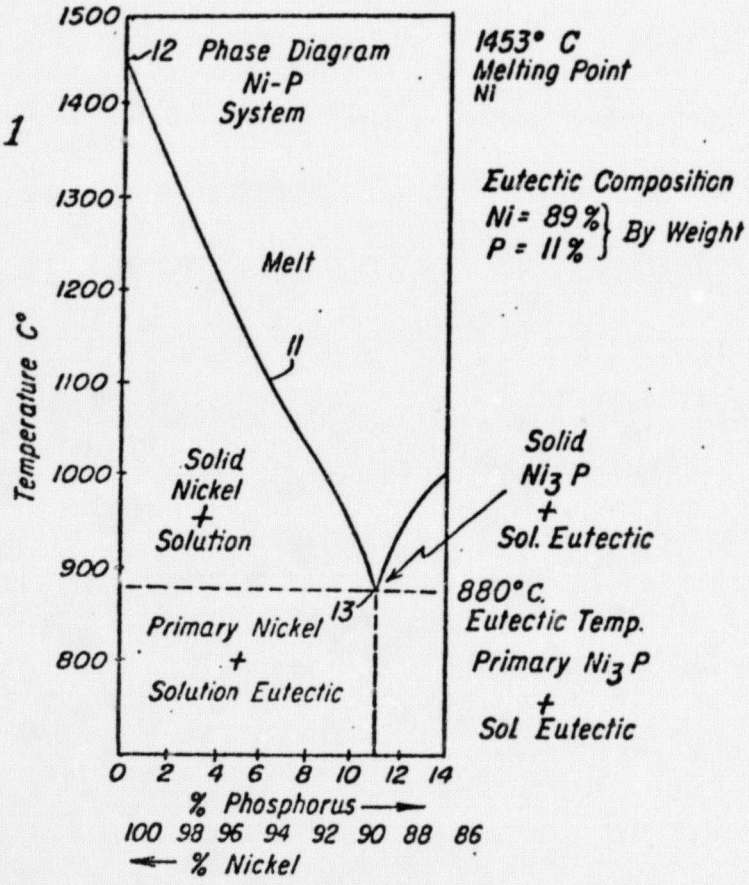
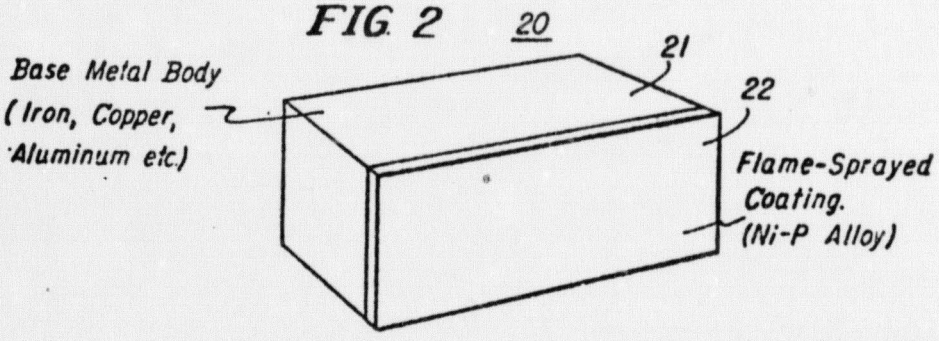


FIG. 2



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E 853

United States Patent Office

2,908,589

Patented Oct. 13, 1959

2,908,589

METHOD OF FLAME SPRAYING AN ALLOY AND THE RESULTING ARTICLE

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Application April 16, 1957, Serial No. 653,199

11 Claims. (Cl. 117—46)

The present invention relates to processes of producing coherent coatings involving a nickel-phosphorus alloy.

It is a general object of the invention to provide a coating process utilizing the metallic reaction product of a chemical plating bath of the nickel cation-hypophosphite anion type, and involving flame spraying of the product mentioned, whereby a coherent coating is produced that consists essentially of a nickel-phosphorus alloy.

Another object of the invention is to provide a process of producing a coherent coating upon a base metal body and involving a flame spraying step, wherein the coating consists essentially of a nickel-phosphorus alloy.

A further object of the invention is to provide an improved process of producing a coherent coating of the character noted, wherein the metallic reaction product of a chemical plating bath of the nickel cation-hypophosphite anion type is fed in finely divided form into a reducing flame made by relatively high velocity gases, so that the particles of the reaction product are melted and the resulting melt is projected by the flame onto a surface to produce a coherent coating thereon, and wherein the reaction product and the coating have fundamentally different physical characteristics and properties.

Further features of the invention pertain to the particular composition of the nickel-phosphorus alloy coating and to the steps of the process of making the same; whereby the above-outlined and additional operating features thereof are attained.

The invention, both as to its organization and method of operation, together with further objects and advantages thereof, will best be understood by reference to the following specification taken in connection with the accompanying drawing, in which:

Figure 1 is a phase diagram of the nickel-phosphorus system, as far as it is pertinent to the nickel-phosphorus alloys that are produced in the coherent coatings, in accordance with the present invention, and illustrating the mutual relationships among phase, temperature and composition of these nickel-phosphorus alloys; and

Fig. 2 is a perspective view of a base metal block carrying on one surface thereof a coherent flame sprayed coating consisting essentially of a nickel-phosphorus alloy of the character noted.

Before proceeding with the description of the present invention, it is first noted that in the operation of a continuous chemical nickel plating system of the character of that disclosed in U.S. Patent No. 2,658,839, granted on November 10, 1953, to Paul Talmey and William J. Crehan, there is employed a plating bath of the nickel cation-hypophosphite anion type; and in the plating operation nickel cations are reduced to metallic nickel and deposited upon the catalytic surface of the object undergoing the chemical nickel plating operation, and hypophosphite anions are correspondingly oxidized to phosphite anions and accumulate in the plating bath. In accordance with the method of Talmey and

Crehan, the plating bath is continuously or periodically regenerated by the addition of nickel cations and hypophosphite ions, thereby to compensate the same for the depletion of these ions resulting from the plating reactions mentioned. Also, these plating reactions in the plating bath are productive of hydrogen ions, whereby hydroxyl ions are added in the regeneration to maintain the desired pH of the plating bath.

While this method greatly extends the useful life of the plating bath, it does not prevent the build-up of phosphite anions and alkali metal salts therein (assuming that the regeneration involves the addition of nickel sulfate, sodium hypophosphite and sodium hydroxide); whereby ultimately it is necessary to discard the used plating bath, as a result of the build-up of high concentrations therein of phosphite anions, sulfate anions and sodium cations, or alternatively to subject the used plating bath to complete chemical "clean-up," as disclosed in the copending application of Paul Talmey, Gregoire Gutzeit and Donald E. Metheny, Serial No. 576,931, filed April 9, 1956.

Specifically, care must be exercised in this connection to prevent precipitation of nickel phosphite in the plating bath, since such precipitate serves as growth nuclei for the formation of "metallic precipitate" therein, with the resulting "random decomposition" of the plating bath. Specifically, the reactions involving the formation of the metallic precipitate in the plating bath are autocatalytic; whereby the formation of any substantial metallic precipitate therein effects the total decomposition of the plating bath very quickly and throughout the body thereof entirely at random and altogether independently of the catalytic surface of the body undergoing the plating operation.

Thus a chemical nickel plating bath becomes "spent" when the phosphite anion concentration therein approaches the threshold of insolubility of nickel phosphite, and must be discarded so as to prevent the possibility of random decomposition thereof in the plating system.

The spent chemical nickel plating bath contains valuable nickel, hypophosphite and phosphite, as well as sodium and sulfate; whereby it is ordinarily subjected to gross nickel salvage by treatment that induces decomposition thereof, the residue of the plating bath comprising an aqueous liquid having the previously-mentioned metallic precipitate suspended therein. The matter of the treatment of the spent chemical nickel plating bath to induce decomposition thereof is exceedingly easy, as this phenomenon involves the previously-mentioned reactions that are autocatalytic; whereby the reactions, once initiated, rapidly spread throughout the plating bath and to the two ingredients (nickel cations and hypophosphite anions) with the formation therein of the metallic precipitate mentioned. Thus, all of the nickel cations in the plating bath are depleted in the presence of the normal slight excess of hypophosphite anions; whereby the subsequent recovery of the metallic precipitate from the aqueous liquid effects the complete recovery of the nickel cations from the residue of the spent chemical nickel plating bath.

The initiation of the reactions mentioned is also exceedingly simple as it is noted that a chemical nickel plating bath is normally in a metastable state, and is subject to catalyzed decomposition. Specifically, the simplest procedure of initiating the reactions is to seed the spent chemical nickel plating bath with a small quantity of previously produced metallic precipitate or a small quantity of any catalytic material in finely divided form, such as iron, cobalt, nickel, palladium, etc. Palladium is highly catalytic and may be employed even

in the form of an aqueous solution of a salt thereof, such as the chloride, nitrate, etc. Also, the reaction rate in the spent chemical plating bath may be enhanced by appropriate increasing the pH thereof, by raising the temperature thereof to the boiling point, etc. Since the reactions are autocatalytic, as previously noted, it is very convenient, as a matter of manipulation, to initiate the same in a small quantity of the spent chemical nickel plating bath contained in a beaker, or the like, and then return the contents of the beaker into the vat or tank containing the bulk of the spent chemical nickel plating bath, thereby seeding the reactions in the bulk of the spent chemical nickel plating bath, in an obvious manner.

This metallic precipitate has been discovered to be an amorphous solid comprising a metastable supercooled solution of phosphorus in nickel, and having no specific composition, but normally containing as produced incident to the random decomposition of a chemical nickel plating bath of the nickel cation-hypophosphite anion type, constituents comprising about 88 to 94% nickel and 6 to 12% phosphorus by weight. The phosphorus content is affected by the pH and by the excess of both hypophosphite anions and phosphite anions in the spent chemical nickel plating bath, but only within the narrow range mentioned. Specifically, a high hypophosphite anion content, in the spent chemical nickel plating bath insures that incident to random or induced decomposition thereof the metallic precipitate produced will have a high phosphorus content within the narrow range, whereas a high phosphite anion content has only a slight effect in this regard. The metallic precipitate produced incident to the random decomposition of a pure simple freshly prepared standard aqueous solution of nickel sulfate and sodium hypophosphite always contains phosphorus in the range 6 to 12% by weight, frequently has a phosphorus content as high as 10% by weight, and occasionally has a phosphorus content as high as 12% by weight. This phenomenon is not really understood, as the random decomposition of the same standard solution in two separate batches is not necessarily productive of identical samples of metallic precipitate as to phosphorus content.

It has been discovered that this metallic precipitate has a melting temperature in the range 880° C. to 1100° C. depending upon composition; whereby the nickel and phosphorus constituents are in equilibrium.

These considerations will best be understood by reference to Figure 1 of the drawing, wherein there is illustrated a portion of the nickel-phosphorus system that is pertinent to the nickel-phosphorus compositions produced by the melting of the precipitate noted. Specifically, it was discovered that the eutectic composition comprises nickel and phosphorus constituents containing about 89% nickel and 11% phosphorus by weight, and that the eutectic temperature is about 880° C. On the curve 11 the melting point of nickel (1453° C.) is indicated at 12 and the eutectic point is indicated at 13. Also, from the curve 11, it will be observed that a composition containing about 5% phosphorus has a melting point of about 1150° C., a composition containing about 6% phosphorus has a melting point of about 1100° C., a composition containing about 10% phosphorus has a melting point of about 950° C., and a composition containing about 12% phosphorus has a melting point of about 950° C.

The eutectic composition of the system is not completely determined, since it appears that it involves fundamentally nickel and phosphorus, and since the proportions by weight are not in accordance with Dalton's law; however, after heat-treatment above 400° C., only nickel and Ni_3P in the alloy have been detected by X-ray diffraction analysis.

All of the compositions that are produced by melting of the metallic precipitate noted contain nickel and phosphorus in the previously-mentioned range by weight (about 88–94% nickel and 6–12% phosphorus); and most of the compositions fall in the even more limited range containing about 90–93% nickel and 7–10% phosphorus by weight. Thus, it will be understood that when the metallic precipitate is heated to a temperature sufficiently high to melt the same, a melt is produced in which the nickel and phosphorus constituents are in equilibrium above the curve 11 of the phase diagram of Fig. 1. Upon subsequent cooling, the melt becomes supersaturated with nickel in the event the phosphorus content of the composition is below 11%; whereas upon subsequent cooling, the melt becomes supersaturated with Ni_3P in the event the phosphorus content of the composition is above 11%. Specifically, in the event there is a deficiency of phosphorus the melt becomes supersaturated with nickel, upon subsequent cooling; whereby solid nickel is formed in the eutectic solution as the composition of the solution moves downwardly and toward the right along the curve 11 and toward the eutectic point 13; hence, when the cooling of the melt proceeds to the eutectic temperature of about 880° C., considerable solid nickel is present in the solution of the eutectic composition, so that upon further cooling of the mass, this solid nickel is productive of primary nickel crystals in the mass of the eutectic composition that appear as substantial nickel dendrites in the eutectic matrix. Specifically, in the event there is an excess of phosphorus, the melt becomes supersaturated with Ni_3P, upon subsequent cooling; whereby solid Ni_3P is formed in the eutectic solution as the composition of the solution moves downwardly and toward the left along the curve 11 and toward the eutectic point 13; hence, when the cooling of the melt proceeds to the eutectic temperature of about 880° C., considerable solid Ni_3P is present in the eutectic composition, so that upon further cooling of the mass, this solid Ni_3P is productive of primary Ni_3P crystals in the mass of the eutectic composition that appear as small crystals of Ni_3P dispersed in the eutectic matrix. Accordingly, it is the melting of the metallic precipitate noted, followed by the subsequent cooling and solidifying of the melt, that is productive of the nickel-phosphorus alloy characterized by the eutectic composition having dispersed therein the primary crystals mentioned. As previously noted, in this metallic precipitate, there is normally an excess of nickel in the composition, whereby the nickel-phosphorus alloys produced is normally characterized by the dispersion therein of nickel dendrites.

From a broad point of view, as a matter of definition, the original nickel-phosphorus material resulting directly from the nickel cation-hypophosphite anion reaction (the amorphous solid material described) may be termed an "alloy," although it is not characterized by the eutectic composition noted; however, it is preferable to apply the term "alloy" to the final nickel-phosphorus material that results from the melting and subsequent solidifying of the original material mentioned, since this final material is characterized by the eutectic composition noted. Thus, hereinafter the term "alloy" will be used only to refer to this final material.

Now this nickel-phosphorus alloy is substantially different, as to characteristics and structure, from the solid nickel-phosphorus material that is chemically plated from a plating bath of the nickel cation-hypophosphite anion type and from the solid nickel-phosphorus material of the metallic precipitate. For examples: this nickel-phosphorus alloy is substantially magnetic, whereas the nickel phosphorus plating and the metallic precipitate are substantially non-magnetic; and the specific resistance of this nickel-phosphorus alloy is considerably less than that of the nickel-phosphorus plating or the metallic precipitate. There are also many other physical and structural differences between this nickel-phosphorus alloy and the nickel-phosphorus plating and the metallic precipitate that are not here discussed at length in the interest of brevity.

Moreover, it will be understood that while the metallic precipitate must be melted to effect the production of the nickel-phosphorus alloy described above, it is not necessary to maintain the condition of the melt for any particular time interval.

It has also been discovered that the "stray" plating that may occur in an undesirable manner in a chemical nickel plating system of the character of that of the Talmey and Crehan patent is substantially of the same composition as that of the metallic precipitate previously described; whereby this stray plating that accumulates in the bottom of the tank in which the chemical nickel plating bath is stored, in the filters of the system, etc., may be accumulated and melted in the manner described above, either alone or with the metallic precipitate mentioned, in order to produce the nickel-phosphorus alloy described. In fact, the stray plating is also an amorphous solid comprising a metastable super cooled solution of phosphorus in nickel and having no specific composition, but normally containing, as produced, constituents comprising about 88 to 94% nickel and 6 to 12% phosphorus by weight. Since the metallic precipitate mentioned and the stray plating mentioned are substantially identical, as a matter of composition, they may be melted together in order to produce the unique nickel-phosphorus alloy described.

The salvage method described above is applicable to a wide variety of chemical nickel plating baths, such, for example, as those disclosed in the following U.S. patents: No. 2,532,283, Brenner and Riddell; No. 2,658,841, Gutzeit and Krieg; and No. 2,658,842, Gutzeit and Ramirez.

A preferred chemical nickel plating bath of extremely wide utility is disclosed in the copending application of Gregoire Gutzeit, Paul Talmey and Warren G. Lee, Serial No. 569,815, filed March 6, 1956, now Patent No. 2,822,294, granted on February 4, 1958; this plating bath essentially comprising an aqueous solution of a nickel salt, a hypophosphite, a complexing agent selected from the group consisting of lactic acid and salts thereof, and an exalting additive selected from the group consisting of propionic acid and salts thereof. In this plating bath, the absolute concentration of hypophosphite ions is within the range 0.15 to 1.20 mole/liter, the ratio between nickel ions and hypophosphite ions is within the range 0.25 to 1.60, the absolute concentration of lactic ions is within the range 0.25 to 0.0 mole/liter, the absolute concentration of propionic ions is within the range 0.025 to 0.060 mole/liter, and the pH is within the approximate range 4.0 to 5.6. This particular chemical nickel plating bath is most satisfactory in carrying out a wide variety of nickel plating operations and of course, when it becomes spent, it may be subjected to the salvage method to produce the nickel-phosphorus alloy previously described.

In accordance with the present method, the previously described reaction product (the metallic precipitate or the stray plating) is recovered from a chemical plating bath of the nickel cation-hypophosphite anion type, as previously described, and then subjected to suitable treatment to produce a finely divided dry powder therefrom. Specifically the reaction product mentioned is first suitably dried and then, if desired, crushed in a jaw crusher, followed by further reduction in a roll grinder, followed by still further reduction in a ball mill. The powdered product of the ball mill comprises a particle size in the general range —200 to —325 mesh. Next the powdered product is treated with a suitable mineral acid in order to leach therefrom all traces of iron and other like impurities, a 5% sulfuric acid solution being adequate for this purpose. The product is then suitably dried and screened so that it is suitable for subsequent use.

This powder is then fed into a reducing flame made by relatively high velocity gases, for instance, in accordance with the Schoop process (see U.S. Patent No. 1,128,059 granted on February 9, 1915, to Max U. Schoop); and specifically this powder may be fed into a conventional powder flame-spray gun, such, for example, as the "Schori" gun, "Metco" gun, etc.; whereby the particles are melted and the resulting melt is projected by the flaming gases from the gun at a relatively high velocity. The gun is directed so that the projected melt impinges upon a surface to be coated; whereby it adheres thereto forming a coherent coating thereon. In the process, the finely divided particles of the amorphous solid supercooled solution of phosphorus in nickel are melted in the reducing flame, and the small globules of the resulting melt are hurled or projected onto the surface to be coated so that they accumulate and cohere, as well as adhere, thereon; whereby upon cooling and resolidification, the previously described nickel-phosphorus alloy is produced in the resulting coating. Thus it will be understood that the finely divided amorphous nickel-phosphorus material that is fed into the flame-spray gun and the nickel-phosphorus alloy of the coating are fundamentally different from each other, both as to structure and physical properties, as previously explained.

For example, the article of manufacture 20 shown in Fig. 2 may be made in accordance with the above-described process. Specifically, the article 20 comprises a base metal body 21 formed of iron, copper, aluminum, etc., and a flame sprayed coherent coating 22 formed of the nickel-phosphorus alloy previously described.

The Schori gun "Model L" operated satisfactorily under the following working conditions:

Acetylene	lb. sq. in.	16
Oxygen	lb. sq. in.	22
Air	lb. sq. in.	10
Powder-feed rate	gm./min.	16–20
Best gun distance from surface undergoing coating	in.	6–8

The Metco gun "Model E" operated satisfactorily under the following working conditions:

Acetylene	lb. sq. in.	10
Oxygen	lb. sq. in.	8
Air	lb. sq. in.	10
Nitrogen (fed)	lb. sq. in.	5
Powder-feed rate	gm./min.	20
Best gun distance from surface undergoing coating	in.	6–8

The utilization of these two flame-spray guns is in no way critical, as they were employed entirely as a matter of convenience; and it will be understood that any conventional flame-spray gun may be employed. In the operation of the flame-spray gun, a reducing flame should be maintained by maintaining a slight deficiency of oxygen to support complete combustion of the inflammable gas utilized, so as to minimize oxidation of the melted particles projected by the flame onto the surface undergoing the coating step; and while a wide variety of combustion gases may be employed, propane is quite satisfactory for the present purpose.

Of course, it will be understood that in accordance with the present method, a wide variety of materials may be coated including both metallic and non-metallic bodies, and in fact even inflammable bodies formed of plastics, wood, etc., may be coated without burning thereof. However, as a practical matter, the coatings are normally applied to base metal bodies formed of iron, copper, aluminum and the usual alloys thereof; and in the coating of such base metal bodies, it is highly advantageous to prepare the surface thereof prior to the coating or metallizing step. Specifically, the surface must be clean, free from grease, water or other contamination. Moreover, the adhesion of the coating is substantially improved by preliminary grit blasting of the surface.

The composite coherent coating thus produced is normally built-up in layers, each having a thickness in the general range 1 to 2 mils; whereby the composite coating may have any desired ultimate thickness. Like other

Schoop coatings, this coating is somewhat porous; however, the porosity of the coating may be decreased by using relatively small particle sizes in the powder that is fed to the flame-spray gun and by employing relatively higher velocities of the flame in the flame-spray gun. Moreover, after the coating has been produced, the density thereof may be increased by flame polishing with a reducing flame. Furthermore, the general appearance of the coating may be substantially enhanced by wire brushing, grit blasting, polishing, etc. While these coatings in excess of about 10 mils are relatively non-porous to aerated boiling water, the porosity thereof can be further reduced by impregnation with a suitable sealer, such as an organic lacquer or coating agent of the vinyl, etc. type.

The nickel-phosphorus alloy of the coating is very advantageous in that it has a relatively low melting point, normally in the range 880° C. to 950° C., and the phosphorus content thereof acts as a de-oxidizing agent resulting in the capability of the molten droplets or globules to wet most metals even though they are coated with a thin normally unwettable oxide film. For example, base metals containing substantially chromium (the usual stainless steels) are readily wetted by this alloy for this reason; whereby a coherent coating of the character described may be readily flame-sprayed upon a base metal body containing substantial chromium; which coating is characterized by good adhesion, notwithstanding the usual unwettable oxide films carried by such stainless steels following careful cleaning thereof.

Moreover, in order to minimize oxidation of the droplets or globules that are projected by the reducing flame, a suitable fluxing agent may be advantageously incorporated in the powder that is fed into the flame-spray gun. Such fluxing compounds as sodium borate may be employed in small amounts. By this arrangement, the normal oxide content of the alloy (usually about 10 to 15% by weight) in the coating may be reduced.

Also, it has been discovered that a ternary alloy of zinc, nickel and phosphorus may be produced in the manner described by feeding into the flame-spray gun a mixture of finely divided metallic zinc and finely divided reaction product of the character described. In the arrangement, about equal parts by weight of metallic zinc and reaction product are fed, in finely divided form, into the reducing flame; whereby in the coating thus produced there was a ternary alloy of zinc, nickel and phosphorus comprising constituents containing by weight about 50% zinc, 44 to 47% nickel and 3 to 6% phosphorus. Specifically, in the arrangement, a 5 mil composite coating was provided upon a base metal body that comprised a 2 mils inner coating bonded to the base metal body and a 3 mils outer coating bonded to the inner coating, wherein the inner coating was formed of the ternary alloy noted and the outer coating was formed of the binary alloy noted. This composite coating offered very remarkable resistance to corrosion in a salt spray test, indicating a life of about 300 hours.

In view of the foregoing, it is apparent that there has been provided an improved process of producing a coherent nickel-phosphorus coating that may be carried out in a ready manner utilizing the conventional flame spray step of the Schoop method, as well as an improved corrosion-resistant coating comprising a nickel-phosphorus alloy of the character described.

While there has been described what is at present considered to be the preferred embodiment of the invention, it will be understood that various modifications may be made therein, and it is intended to cover in the appended claims all such modifications as fall within the true spirit and scope of the invention.

What is claimed is:

1. The process of producing a coherent coating, which comprises providing finely divided particles of an amorphous solid supercooled solution of phosphorus in nickel and containing about 88 to 94% nickel and 6 to 12% phosphorus by weight and characterized by alloying of the constituents thereof following melting and upon resolidification thereof, wherein said alloy is characterized by an eutectic matrix comprising nickel and phosphorus constituents containing about 89% nickel and 11% phosphorus by weight and having an eutectic temperature of about 880° C., feeding said particles into a reducing flame of relatively high velocity gases, whereby said particles are melted and the resulting melt is projected by said reducing flame, and directing said projected melt onto a surface so as to produce a coherent coating thereon and adhering thereto that consists essentially of said alloy.

2. The process set forth in claim 1, wherein said flame essentially comprises the combustion products of propane and oxygen.

3. The process set forth in claim 1, wherein said particles essentially comprise the solid reaction product of a chemical plating bath of the nickel-reductionhypophosphite anion type.

4. The process set forth in claim 1, wherein said particles essentially comprise the metallic precipitate that is formed incident to the decomposition of an aqueous solution containing nickel cations and hypophosphite anions.

5. The process set forth in claim 1, wherein said particles have a size in the general range —200 to —325 mesh.

6. The process of producing a coherent coating upon the surface of a base metal body, which comprises preparing the surface of said body by cleaning and roughening the same, providing finely divided particles of an amorphous solid supercooled solution of phosphorus in nickel and containing about 88 to 94% nickel and 6 to 12% phosphorus by weight and characterized by alloying of the constituents thereof following melting and upon resolidification thereof, wherein said alloy is characterized by an eutectic matrix comprising nickel and phosphorus constituents containing about 89% nickel and 11% phosphorus by weight and having an eutectic temperature of about 880° C., feeding said particles into a reducing flame of relatively high velocity gases, whereby said particles are melted and the resulting melt is projected by said reducing flame, and directing said projected melt onto the prepared surface of said body so as to produce a coherent coating thereon and adhering thereto that consists essentially of said alloy.

7. The process set forth in claim 6, wherein said base metal contains sufficient chromium to interfere with wetting thereof by molten nickel.

8. The process of producing a coherent coating upon the surface of a base metal body, which comprises preparing the surface of said body by cleaning and roughening the same, providing finely divided particles of an amorphous solid supercooled solution of phosphorus in nickel and containing about 88 to 94% nickel and 6 to 12% phosphorus by weight and characterized by alloying of the constituents thereof following melting and upon resolidification thereof, wherein said alloy is characterized by an eutectic matrix comprising nickel and phosphorus constituents containing about 89% nickel and 11% phosphorus by weight and having an eutectic temperature of about 880° C., feeding said particles into a reducing flame of relatively high velocity gases, whereby said particles are melted and the resulting melt is projected by said reducing flame, directing said projected melt onto the prepared surface of said body so as to produce a layer thereon that consists essentially of said alloy, and then re-melting said layer by directing a flame of gases thereon so that upon resolidification of said layer there is produced a coherent coating upon the surface of said body and adhering thereto.

9. The process of producing a coherent coating upon the surface of a base metal body, which comprises preparing the surface of said body by cleaning and roughen-

ing the same, provi[illegible]inely d[illegible]ed particles of an amorphous solid [illegible]ercooled [illegible]lution of phosphorus in nickel and co[illegible]ing [illegible]t 83 to 94% nickel and 6 to 12% ph[illegible]us by weight and characterized by alloying [illegible]e constituents thereof following melting and [illegible] resolidification thereof, wherein said alloy is char[illegible]terized by an eutectic matrix comprising nickel and phosphorus constituents containing about 89% nickel and 11% phosphorus by weight and having an eutectic temperature of about 880° C., providing finely divided particles of a suitable solid refractory flux, feeding a mixture of said solution particles and said flux particles into a reducing flame of relatively high velocity gases, whereby said solution particles and said flux particles are melted and the resulting melt is projected by said reducing flame, directing said projected melt onto the prepared surface of said body so as to produce a layer thereon that contains both said alloy and said flux, and then remelting said layer by directing a flame of gases thereon so that an underlayer of said alloy and an overlayer of said flux is produced thereon, whereby upon resolidification of said underlayer there is produced a coherent coating upon the surface of said body and adhering thereto.

10. The process of producing a coherent coating, which comprises collecting the metallic reaction product from a chemical plating bath of the nickel cation-hypophosphite anion type, finely dividing said metallic reaction product to produce a particle size in the general range —200 to —325 mesh, washing said finely divided particles with an aqueous solution of a mineral acid to remove foreign impurity therefrom, drying said finely divided particles, feeding said dry finely divided particles into a reducing flame of relatively high velocity gases, whereby said particles are melted and the resulting melt is projected by said reducing flame, and directing said projected melt onto a surface so as to produce a coherent coating thereon and adhering thereto that consists essentially of a nickel-phosphorus alloy.

11. The process set forth in claim 6, wherein said base metal body is formed essentially of steel.

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E 858

Oct. 27, 1959 E. M. GRALA ET AL 2,910,356

CAST NICKEL ALLOY OF HIGH ALUMINUM CONTENT

Original Filed July 19, 1956 3 Sheets-Sheet 3

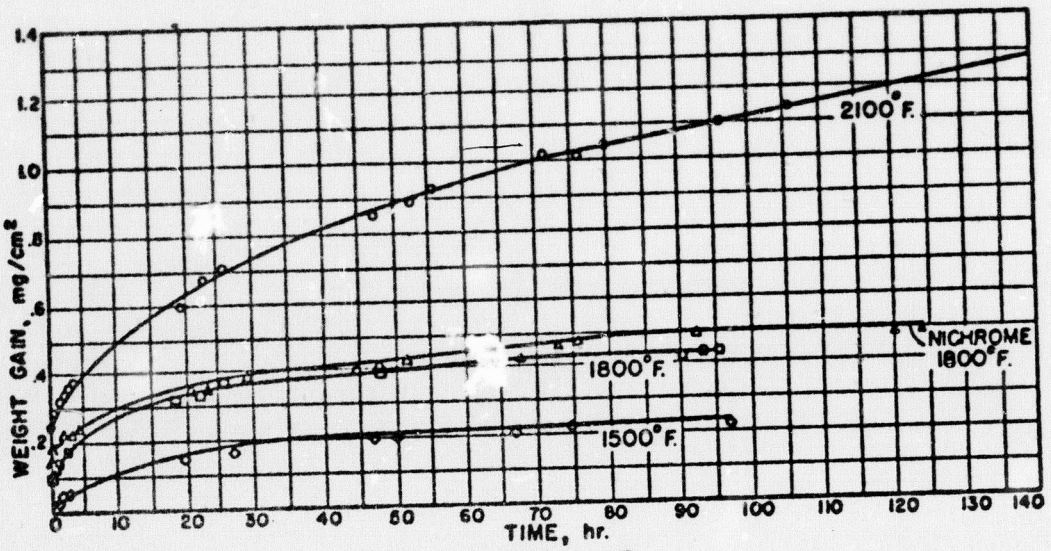

FIG. 5

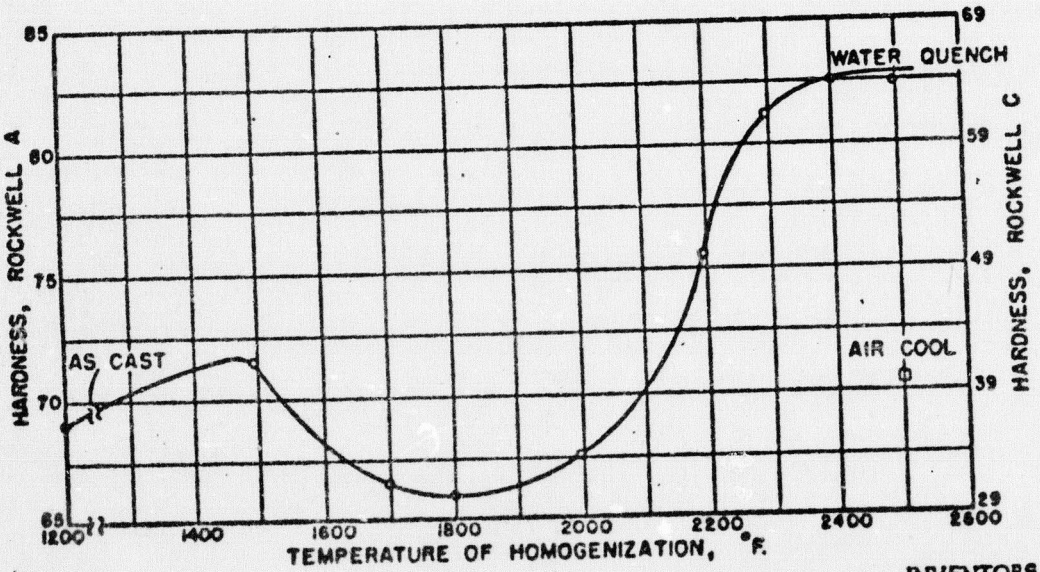

FIG. 6

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CAST NICKEL ALLOY OF HIGH ALUMINUM CONTENT

Original Filed July 19, 1956 3 Sheets-Sheet 2

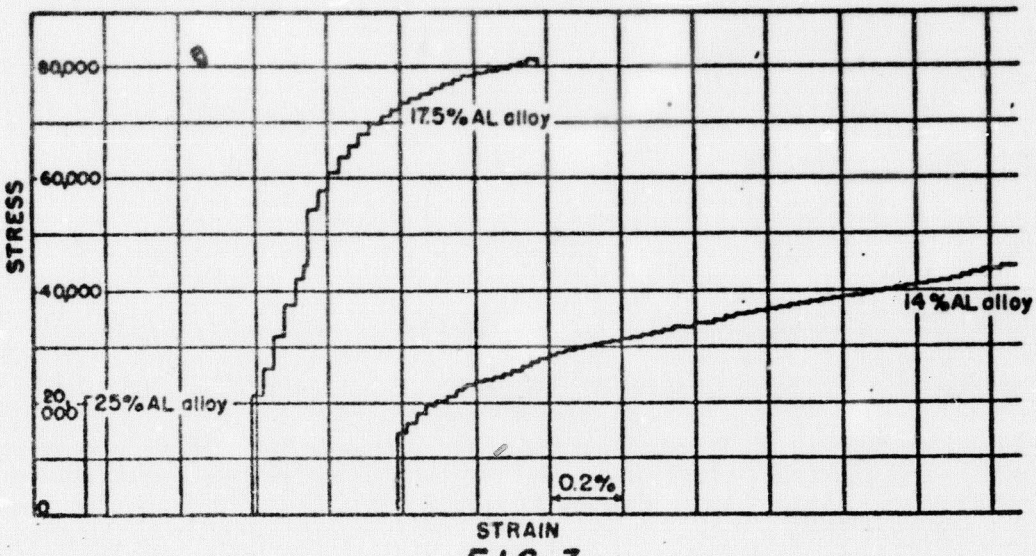

FIG. 3

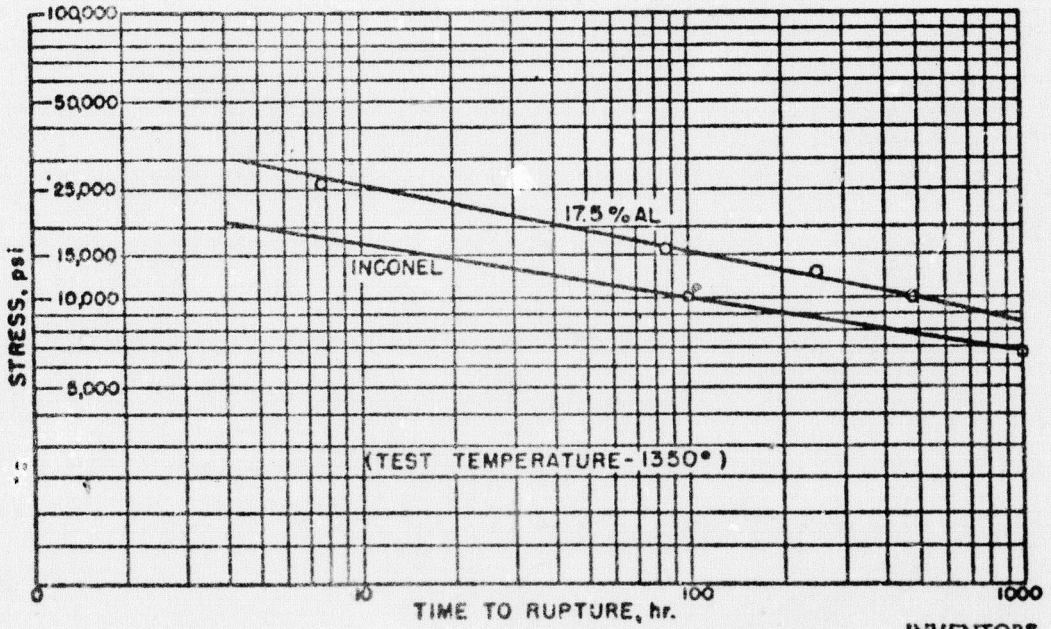

FIG. 4

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Oct. 27, 1959 E. M. GRALA ET AL 2,910,356

CAST NICKEL ALLOY OF HIGH ALUMINUM CONTENT

Original Filed July 19, 1956 3 Sheets-Sheet 1

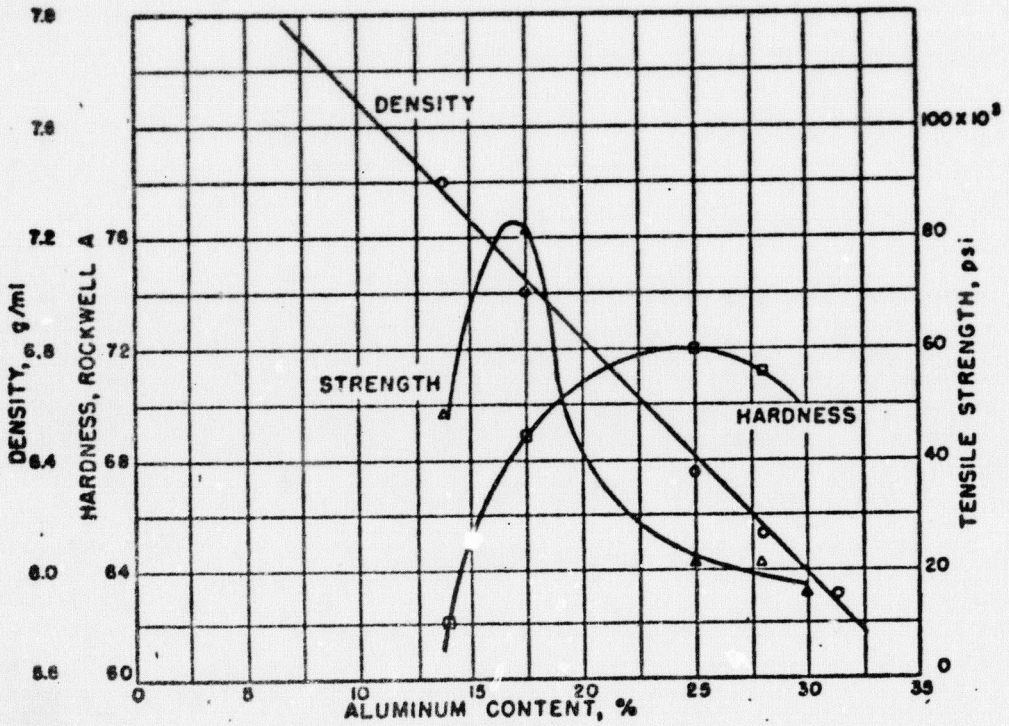

FIG. 2

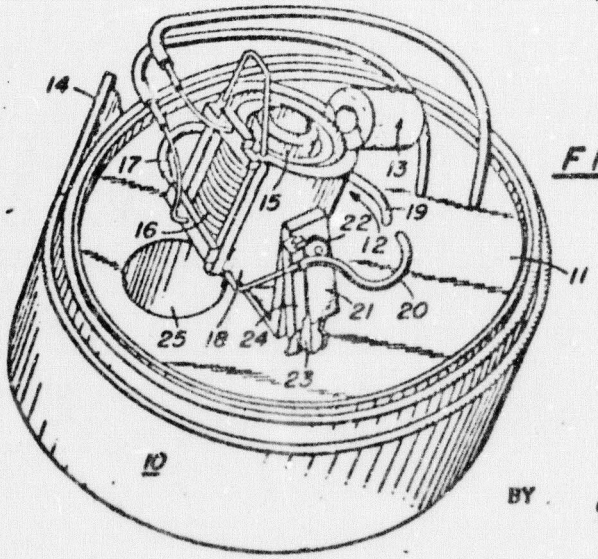

FIG. 1

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United States Patent Office 2,910,356
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2,910,356

CAST NICKEL ALLOY OF HIGH ALUMINUM CONTENT

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Original application July 19, 1956, Serial No. 532,128. Divided and this application October 16, 1956, Serial No. 616,355

1 Claim. (Cl. 75—170)

(Granted under Title 35, U.S. Code (1952), sec. 266)

The invention described herein may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to cast nickel aluminum alloys in which the aluminum is present in amounts in excess of 10 percent by weight.

Intermetallic compounds, such as the nickel-aluminum compound NiAl, are known to possess properties radically different from those of their constituent elements. In the case of NiAl, for example, the melting point is high compared with that of nickel and aluminum, and there are important differences over the constituent metals in modulus-of-rupture strengths and oxidation resistance at high temperatures. The intermetallic Ni_3Al also possesses distinctive properties.

NiAl intermetallic compositions have been prepared heretofore by the methods of powder metallurgy, casting methods resulting in extremely weak, porous and fragile bodies, due primarily to the high exothermic heat developing in the mass. The present invention contemplates a casting procedure for nickel-aluminum mixtures with the aluminum in excess of 10% and, particularly, in the 14–30% range in which the exothermic temperatures are controlled by the particle size of the mixed metals, by the method of heating, and by the sequence of treatment during heating.

An outstanding object of the invention is to provide a cast nickel-aluminum composition which contains intermetallic phase alloys and which possesses high tensile strength both at room and high temperatures. Another object is to provide a cast alloy of nickel and aluminum, containing at least 10 percent aluminum, which may be hot rolled. Still another object is to provide a cast nickel-aluminum alloy containing about 14 to 30 percent aluminum which, at high temperatures, is thermal-chock resistant and hard, possesses adequate impact strength and resists oxidation.

Additional objects are to provide a nickel-aluminum alloy with at least 14 percent aluminum which serves readily as a base for additional metal alloys, and which eliminates use of fluxes in the alloy casting process.

Other objects and many of the attendant advantages of this invention will be readily appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings wherein:

Fig. 1 is a perspective view of the crucible and mold unit partly tilted toward pouring position;

Fig. 2 is a set of curves showing change of hardness, density and tensile strength for different values of aluminum content of the nickel aluminum alloy;

Fig. 3 is a set of stress-strain curves showing the ductility of the nickel-aluminum alloy for different selected percentages;

Fig. 4 is a set of curves showing the stress-time-to-rupture values of the nickel-aluminum alloy as compared with Inconel;

Fig. 5 is a set of curves indicating oxidation effects of the alloy for different temperatures and in comparison with Nichrome; and

Fig. 6 is a curve showing the variation of hardness of the nickel-aluminum alloy having 17.5 percent aluminum, with variation in the temperature of homogenization.

In the manufacture of the alloy, the castings are prepared in a bell-jar vacuum induction furnace unit, as illustrated in Fig. 1, including the support casing 10, the base plate 11, and induction furnace 12, the mold 13 and the bell-jar 14. The furnace comprises a tubular, refractory, alumina crucible 15, having an open top end for reception of the metal charge, an enclosing tubular coil 16 of an electrical conductor 17 serving to impart inductive heating flux to the metallic crucible contents, and a cooling jacket 18, provided with coolant connections 19 and 20, surrounding the coil 16. The furnace is mounted pivotally on upright stanchions 21, one of which is shown in Fig. 1. The pivot rod terminates in a pinion 22 external to stanchion 21; and a rack 23, movable in sleeve 24 by mechanism (not shown) placed in the support casing 10, serves to rotate the crucible through a limited arc of movement for discharge of the molten metal.

For convenience, and to eliminate spillage, the mold for the casting is attached to the upper edge of jacket 18, mid-point between the pivot points and on the side of the crucible which is below on pouring movement. The mold is secured detachably to the jacket so as to extend at right angles to the crucible axis, and, when the crucible is tipped, liquid in the crucible flows directly into the upper mold 13 where it is solidified by cooling to room temperature.

In order to prevent oxidation of the molten aluminum, air is withdrawn from the crucible space in bell-jar 14 through the vacuum opening 25 in the base 11 which communicates with the vacuum pump through casing 10. Also, to prevent the molten aluminum from vaporizing, a slight positive pressure of an inert gas, such as argon, is maintained within the bell-jar.

The raw materials used in the charge are electrolytic nickel (99.95% purity) and 2S aluminum (99.0+% purity). It is desirable that the nickel be prepared, not as a powder or grain, but in the form of discrete fragments or particles and preferably in the form of small flat chips; and the aluminum is used in small fragments or pieces of 1-inch diameter bar stock. In a typical treatment the nickel chips are placed on the bottom of the crucible and the aluminum bar pieces over the nickel. When the alternating furnace current is turned on, the nickel acts as a susceptor in the induction field and raises the aluminum temperature to the melting point. The reaction between the molten aluminum and solid nickel is strongly exothermic, especially, for high-aluminum alloys, as 20 to 30 percent aluminum, and the charge becomes molten in a few seconds, where the initial charge weight is in the neighborhood of 400 to 600 grams. The melt is stirred effectively by both the chemical reaction and the induction field. About 1 minute after the start of the reaction (for the charge mentioned) the melt is poured into the mold. This is not a limiting or critical time period as the holding time may be extended, but the time should be definite and not be extended unnecessarily because of the tendency to vaporization and danger of contamination by the crucible material. The mold substance is preferably copper in order to give a chill cast effect, but a ceramic mold is feasible although producing a larger grain size in the casting.

Close control over the process during the melting and reacting of the constituent metals is obtained by control of the size of the aluminum and nickel particles in the charge, the larger the pieces, generally considered, the better the control. The dissolving of the solid nickel into

the molten aluminum retards the violence of the reaction and keeps the maximum temperature of the reaction down. In the case of powders, not only is the reaction much more violent, but the gases entrapped in the powder briquette during the cold pressing operation are involved during the reaction and produce large pores in the fused mass. Consequently, this porous mass must be ground into powder and fabricated into useful form by powder metallurgy methods.

The nickel-aluminum alloy has been described as containing 14 to 30 percent aluminum. This range is of interest since, heretofore, castings of this alloy in the specified range possessing adequate tensile strength, thermal shock and oxidation resistance and other desired properties have not been obtainable. In addition, this range includes the intermetallic phases NiAl and Ni_3Al, and tests on these substances, as made by powder metallurgy methods, show these alloys to have desirable properties. In order to ascertain the properties of the alloy, cast as described hereinabove, a series of alloys with different aluminum percentages, was examined as to hardness, tensile strength and density, and graphs showing these properties are found in Fig. 2. These graphs show a linear decrease of density with increase of aluminum; an increase in hardness up to about 25 percent aluminum, followed by a decrease; and a pronounced peak in tensile strength at an aluminum percentage of 17.5, in the alloy. On examination of the structure of this 17.5 percentage alloy by X-ray techniques, it is found to correspond to the NiAl plus Ni_3Al phases of the nickel-aluminum phase system, Ni_3Al being the intermetallic phase containing approximately from 13.3 to 16 percent aluminum and NiAl being the intermetallic phase containing approximately from 24 to 36.5 percent aluminum at room temperature.

It is pointed out that the 17.5 percent aluminum alloy not only possesses marked tensile strength amounting to 79,600 pounds per square inch at room temperature, but also the hardness and density are substantial. In Figs. 3 to 6 are graphs showing other properties of the 17.5 percent aluminum alloy. Fig. 3 illustrates the stress-strain characteristic of the alloy to the rupture point, not only for the 17.5 percent aluminum alloy but also for alloys containing 14 and 25 percent aluminum, the values corresponding to the intermetallic phases NiAl and Ni_3Al, respectively. Fig. 4 illustrates the stress-to-rupture time for the 17.5 percent aluminum alloy as compared with Inconel, a refractory alloy capable of uses parallel to the described alloy. Fig. 5 shows graphs descriptive of oxidation properties of the described 17.5 percent alloy as compared to Nichrome, both at 1800° F. The oxidation gain of the 17.5 percent alloy at temperatures of 1500° F. and 2100° F. is also shown. Fig. 6 illustrates the effect of homogenization treatment on the 17.5 percent aluminum alloy for temperatures varying from 1200° F. to 2500° F. the alloy being held at selected temperatures for a number of hours, as 48 hours, bringing about elimination of as-cast heterogeneities, changes in composition of the Ni_3Al and NiAl phases and changes in the relative quantity of each phase. The phase changes are apparent from examination of photomicrographs, indicating a progressive solution of the Ni_3Al phase in the NiAl phase which becomes complete around 2400° F. Beginning around 2200° F., also, a needle-like martensite structure appears in the grains on cooling, which appears to be closely related to the increase in hardness as shown in Fig. 6.

It is noteworthy that at 2400° F. where all phases of the 17.5 percent-aluminum alloy have transformed to NiAl, the alloy could be readily hot-rolled, a reduction of 15.9 percent per pass being sustainable. Much smaller values of reduction were obtainable for this alloy at 2200° F. and 2100° F. amounting to 3.9 and 2.1 percent, respectively. The only other alloy susceptible to successful hot-rolling is the 28 percent aluminum alloy, a crack-free reduction per pass of 3.3 percent being obtainable at 2600° F. In this hot-rolling procedure, about 3 seconds were required to remove the ingots, to be rolled, from the furnace to the rolls. Even though the cold rolls act as a quenching medium, the centers of the ingots are untransformed NiAl, as appears from microscopic examination of polished specimens of rolled material. The fact that the alloy was able to sustain an approximately 16 percent reduction indicates that the untransformed NiAl phase is plastic.

The room-temperature tensile strength of the 17.5 percent aluminum alloy rolled to 10% reduction is 73,400 pounds per square inch, and with 50 percent rolling, 86,300 pounds per square inch. It is further noted that homogenization treatment of the as-cast 17.5 percent-aluminum alloy at 2400° F. increases the tensile strength to 94,250 pounds per square inch, with no elongation. In addition, it is important to note that the tensile strength of the alloy is retained at elevated temperatures. For example, at 1500° F. the 17.5 percent aluminum alloy has a tensile strength of 52,900 pounds per square inch (p.s.i.), as cast. Homogenized for 48 hours at 2000° F., the tensile strength is increased to 55,250 p.s.i. Rolled 50 percent at 2400° F. the tensile strength becomes 50,000 p.s.i. As cast, with 0.5 percent molybdenum added, the tensile strength becomes 52,600 p.s.i. and rolled 34 percent at 2400° F., with 5.0 percent molybdenum added, the tensile strength is 55,000 p.s.i. Of interest also is the ductility of the alloy, the values of elongation in percent for the as-cast alloy at room temperature and as-cast alloy at 1500° F. being, respectively, 0.6 and 2.9 percent, the homogenized alloys (48 hours at 2000° F.) for room temperature and 1500° F. being respectively, 0 and 2.5 percent, and the hot-rolled alloys (50% and 2400° F.) for room temperature and 1500° F. being, respectively, 0 and 4.4 percent.

The nickel-aluminum alloys, containing from 14 to 30 percent aluminum and prepared as castings with or without subsequent hot working, not only possess desirable properties such as high strength, corrosion resistance and low specific gravity but also are formed of metals readily available as distinguished from the expensive alloying agents such as cobalt, chromium and niobium. Since the alloy is corrosion resistant at room temperature it may be used, for chemical equipment and dental supplies. It is, also, important to note that, if found desirable, strengthening, gain refining or deoxidizing agents may be added to the nickel-aluminum alloy, without diminishing the alloy strength, such as boron, carbon, calcium, lithium, titanium, molybdenum, the rare earths, silicon, zirconium, vanadium, niobium, tantalum and iron. For example, the tensile strength of 17.5 percent-aluminum alloy at room temperature is increased from 83,800 pounds per square inch to 88,600 pounds per square inch by the addition of 5.0 percent molybdenum, and to 92,600 pounds per square inch by the addition of 0.05 percent boron.

Special attention has been given to the 17.5 percent-aluminum alloy because of its outstanding tensile strength and hot-rolling capability. However, alloys with other aluminum percentages above 10 percent have desirable values, as indicated by the typical room temperature data in the following table.

Chemical composition, percent		Phases present	Tensile strength	Elongation	Hardness Rockwell A	Density, g./ml.
Ni	Al					
86	14	Ni_3Al	80,000	6.8	62	7.39
82.5	17.5	Ni_3Al-NiAl	93,800	0	69	6.99
75	25	NiAl	24,100	0	72	6.33
72	28	NiAl	20,000	0	71	6.12
70	30	NiAl	16,300	0	----	5.98

Obviously many modifications and variations of the

present invention are possible in the light of the above teachings. It is therefore to be understood that within the scope of the appended claim the invention may be practiced otherwise than as specifically described.

This application is a division of copending application No. 532,128, filed July 19, 1956.

What is claimed is:

A nickel-aluminum alloy casting having the combination of superior hot formability, strength, room-temperature and 1500° F. ductility, oxidation resistance and stress-to-rupture time, said casting being composed of an alloy consisting of the two phases Ni_3Al and NiAl with about 17.5 percent aluminum, said casting being produced by forming the nickel in small discrete chips, forming the aluminum in pieces each larger than each of said nickel chips, placing the nickel chips and aluminum pieces in an induction furnace in contiguous overlying layers, introducing an inert atmosphere into said furnace at a pressure in excess of atmospheric, melting said aluminum prior to melting said nickel by applying electromagnetic flux to said nickel said nickel chips thereupon dissolving into the molten aluminum and reacting therewith to form said alloy and pouring said molten alloy into a mold external to said furnace said mold being at a temperature below that of said furnace, an inert atmosphere at a pressure in excess of atmospheric being continuously maintained in the apparatus during melting, casting and cooling.

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E 864

United States Patent Office

2,943,951

Patented July 5, 1960

2,943,951

FLAME SPRAYING METHOD AND COMPOSITION

John Helge Hedlund, Hallstahammar, Sweden, assignor to Aktiebolaget Kanthal, Hallstahammar, Sweden, a corporation of Sweden

No Drawing. Filed Mar. 18, 1957, Ser. No. 646,536

Claims priority, application Sweden Mar. 23, 1956

17 Claims. (Cl. 117—22)

This invention relates to flame spray coating fused or partly fused solids onto a surface for protection of the latter or onto the surface of a ceramic body to produce an electric resistor coating thereon or other purposes.

Flame spraying may be effected by projecting a spray of solid metal particles through an oxygen-acetylene flame which fuses or partly fuses the particles. Further, the solid particles may be mixed with particles of iron oxide and aluminum, for example, which react exothermically. However, protection of the surface, normally metallic, against oxidation at high temperatures or the operation of the electric resistor at high temperatures requires the use of highly refractory compounds which inherently involve problems in connection with their application by flame spraying.

The present invention has for its object to utilize flame spraying to apply a coating largely comprising molybdenum disilicide, $MoSi_2$, and if desired one or more of the other highly refractory silicides of the transition metals of groups IV, V and VI [titanium, zirconium, hafnium, vanadium, niobium (or colombium), tantalum, chromium, tungsten], such as, for example, chromium and titanium disilicides, and also silicon carbide.

According to the present invention the individual powder particles of such silicon containing refractories coated with an oxide film of silicon dioxide are mixed with powder particles of a metal, for instance aluminium or magnesium, which has a strongly positive heat of reaction with oxygen in comparison with that of silicon. It should be observed that said silica film is formed already at normal room temperature by the action of the atmosphere as is the case in all base metals. At higher temperatures, such as in flame spraying, the thickness of the silica film will increase. In any case, no special measures need to be taken to coat said powder particles with a silica film.

In the course of the reaction taking place during flame spraying, the oxide film will be reduced whereby good sintering together of the particles sprayed onto the surface will result. The reaction between aluminium and silicon dioxide is exothermic in nature which means that heat will be given off, and the silicon and aluminium oxide formed will be present in a nascent state all of which will highly enhance the sintering together of the surface coating on the object treated. The course of the process described can be further amplified by the addition of a readily reducible pulverulent oxide such as nickel oxide or cobalt oxide both of which have been found to be particularly suitable. This action depends thereon that said oxides give an intense reaction heat with aluminium whereby the reaction products adhering to the surface show an increased superficial activity. The sintering together is thereby facilitated also in respect of the silicon containing product.

When comparing flame spraying with aluminium and iron oxide, and flame spraying with aluminium and silicon dioxide the following points should be considered:

In alumino-thermic reaction processes the heat energy produced is directly related to the heat of formation of the oxides taking part in the process. In the case of reacting aluminium with iron oxide more than twice as many calories are obtained as in the case of silicon dioxide, which in part explains the fact that silicon dioxide and aluminium will not spontaneously react alumino-thermically with each other upon ignition. However, such a reaction, once started, can be sustained by continuously maintaining the temperature at an elevated point by artificial means, such as by flame spraying.

The reaction involving silicon dioxide further distinguishes from that involving iron oxide by the fact that silicon will form a lower oxide (silicon monoxide, SiO), having a boiling point of 1880° C. When reducing silicon dioxide this silicon monoxide may be formed, and when the temperature is about 1880° C. and higher, substantial portions of the silicon dioxide may escape in the form of gasified silicon monoxide, SiO.

Now to enable flame spraying of molybdenum disilicide to be carried out, the temperature must be raised to a point at which the powder particles are fused or, at least, softened so as to be formable, which corresponds to a temperature of about 2030° C. Owing to this elevated temperature at which the alumino-thermic reaction will be sustained, removal of the surface film of silicon dioxide is effected by reduction and/or vaporization whereby exposed clean metallic surfaces are obtained which is a condition required for a satisfactory sintering together of the flame sprayed silicide coating.

The practical applicability of the present invention is illustrated by the following examples, the proportions cited being by weight:

Example 1

A mixture of 92% $MoSi_2$, the granular particles of which are coated with a film of SiO_2 and are of grain sizes ranging between 5 and 10 micra, 5% Al having a grain size of about 40 micra, and 3% cobalt oxide, is mixed with 15+% polyethene and is extruded into a string ⅛ inch in thickness. Such string is excellently adapted for flame spraying using a conventional spray gun and using acetylene and oxygen gas as fuel. Such fuel may be adjusted to give temperatures about the 2030° C. noted above.

Example 2

In a pulverulent mixture of 90% $MoSi_2$, 7% of an aluminium-magnesium alloy (50% Al, 50% Mg) and 3% $TaSi_2$, the silicide grains are coated in advance with a film of SiO_2. The mixture is subjected to sintering in an atmosphere of hydrogen gas at 1200° C. into a structurally uniform product which is then crushed in a ball mill into an average grain size of 20 micra. This powdered mixture is suitable for flame spraying using any equipment adapted for the relevant purpose.

Example 3

For admixing into polyethene for flame spraying purposes as described in connection with Example 1, the following pulverulent mixture is used: 60% $MoSi_2$, 20% $CrSi_2$, 10% SiC, 8% Al and 2% ferroboron (11% B), the silicide and carbide grains being coated in advance with a film of SiO_2.

In the pulverulent mixture, according to the present invention, the grain size of the silicide or silicides is 50 micra or less, preferably 15 micra or less, and the content of aluminum powder is 1 to 10 percent by weight, preferably 2 to 6 percent by weight, of the powder mixture, its grain size ranging between 10 and 150 micra, preferably between 40 and 70 micra.

It has been found by experiments that the amount

and grain size of the aluminum powder has a critical influence on the result obtained by the flame spraying operation. An addition of between 2 and 6% Al will act to minimize the oxide content of the coating obtained, which oxide corresponds to 0 to 5 percent by weight. If the aluminum addition be taken substantially less than 2% or essentially in excess of 6%, the oxide content of the coating will be increased to between 5 and 20%. As a matter of fact, if the aluminum content is less than 2% the coating will have silicon dioxide included into it, and if on the other hand, the aluminum content exceeds 6%, the coating will instead have aluminum oxide included into it. However, with an addition of 1 to 10% aluminum it is possible, as a rule, to obtain fairly satisfactory results.

It is of advantage to have as low as possible an oxide content in the coating, since a high content of oxides will reduce the imperviousness of the coating and will thereby give rise to an intensified oxidation, especially at elevated temperatures. In addition, the mechanical strength of the coating will, as a rule, be lower if the oxide content is high.

The major portion of the aluminum powder added to the mixture will oxidize during the spraying operation and will form an oxide which is blown off as a loss. However, a small proportion of the oxide may remain in the coating. Its content of metallic aluminum will be very low, usually lower than 1%.

As regards the grain size of the aluminum powder, it has been found that grain sizes of 40 to 70 micra will give good results with only a slight oxide content in the coating, whereas aluminum powder having a grain size of 1 to 2 micra will cause substantial oxidation of the surface coating, which would be due to the fact that such finely grained aluminum powder is substantially oxidized even in its initial condition. In any case, the aluminum powder should be coarser than 10 micra but finer than 150 micra.

The grain size of the silicide powder should be related in a determined manner to the quantity of the aluminum powder, in that coarse silicide particles call for less aluminum quantity, it being understood that the coarser are the solid grains the relatively less is the quantity of SiO_2 which means that a less quantity of aluminum is consumed. The grain size of the silicide used should suitably be approximately 15 micra or less, and in any case less than 50 micra. The statement of a grain size of 15 micra or less should be considered to mean that 90% by weight of the material have a grain size less than 15 micra.

When flame spraying a pulverulent silicide without the addition of a strongly positive metal, or a metal which combines actively with oxygen, the spray losses will be very great. This condition would be explained by the fact that in this case the surfaces of the silicide particles will be coated with a layer of silicon dioxide, or any such pre-existent layer will be thickened, which will prevent adhesion of the particles so that the latter will instead be blown off and get lost. If, on the other hand, aluminum powder is added, it is believed that the silicon dioxide will be reduced into silicon monoxide SiO, which is volatile and thus will volatilize whereby the silicide surface will be metallic and more prone to facilitate the sintering together. However, this less of silicon monoxide implies a lowering of the silicon content of the silicide. When spraying tungsten and molybdenum silicides the highly volatile oxides MoO_3 and WO_3 will boil off but to a less extent than would be required in order to compensate for the loss in silicon. Therefore, also when using molybdenum and tungsten silicides, the flame sprayed coating will be found to have a silicon content which is lower than that of the raw materials.

When flame spraying a mixture of molybdenum disilicide plus 3% aluminum powder the loss in silicon involved will be of such a magnitude that the composition of the coating will correspond to the formula $MoSi_{1.3}$. This composition corresponds to the eutectic between the compounds $MoSi_2$ and Mo_5Si_3. The losses of molybdenum trioxide and silicon monoxide involved in such an experiment means that the total recovery will amount to no more than 30% of the theoretically possible value. However, if aluminum powder should not be added, the recovery would be very much reduced and would only amount to 4 to 6%. If the powdered mixture contains a silicon content lower than that corresponding to the formula $MoSi_2$, then the silicon content of the coating obtained will be still lower than in the initial materials, and at the same time a certain amount of Mo_3Si will form. Since the resistance to oxidation of this silicide is materially lower than that of the other two molybdenum silicides, the resistance to oxidation of the coating at elevated temperatures will be low.

Example 4

For admixing into polyethene for flame spraying purposes as described in connection with Example 1, the following pulverulent mixture is used: 97% molybdenum silicide composed by 45% Si and 55% Mo and having grain sizes less than 10 micra, and 3% aluminum with finer grains than 325 United States mesh.

The higher Si content in the silicide in this example has for its purpose to compensate for the Si losses in the spraying. The composition of the coating obtained is nearly pure $MoSi_2$ (i.e. 37% Si and 63% Mo) and Al_2O_3 and a small amount of oxide.

What is claimed is:

1. A composition for flame spraying on a surface to apply a coating largely comprising a silicide of molybdenum, said composition including a refractory component comprising at least one compound selected from the group consisting of refractory silicon compounds of the transition metals of the fourth, fifth and sixth groups of the periodic table and carbon, said refractory component at least largely comprising a silicide of molybdenum and being in the form of powder particles which when exposed to the atmosphere automatically form coating films of silicon dioxide interfering with their adhesion together; and a metallic component in the form of powder particles of a metal having a strongly positive heat of reaction with oxygen in comparison with that of silicon and which is effective at flame spraying temperatures at least softening said silicide to reduce said silicon dioxide films and expose clean surfaces for adhesion together of said refractory component powder particles, said component powder particles being intermixed.

2. The composition of claim 1 in which said silicide of molybdenum of said refractory component has a higher content of silicon than the desired silicon content of the flame sprayed coating.

3. The composition of claim 2 in which said metal comprises aluminum.

4. The composition of claim 2 in which said metal comprises aluminum and constitutes from 1 to 10% by weight of the mixture of said components.

5. The composition of claim 2 in which said refractory component has a grain size not greater than 50 microns and said metallic component has a grain size ranging between 10 and 150 micra.

6. The composition of claim 1 in which said refractory component also comprises a silicide of tungsten and it and said silicide of molybdenum of said refractory component have higher silicon contents than the desired silicon content of the flame sprayed coating.

7. The composition of claim 6 in which said metal comprises aluminum.

8. The composition of claim 6 in which said metal comprises aluminum and constitutes from 1 to 10% by weight of said components.

9. The composition of claim 6 in which said refrac-

tory component has a grain size not greater than 50 micra and said metallic component has a grain size ranging between 10 and 150 micra.

10. The composition of claim 1 in which said metal comprises aluminum.

11. The composition of claim 1 in which said metal comprises aluminum and constitutes from 1 to 10% by weight of the mixture of said components.

12. The composition of claim 1 in which said refractory component has a grain size not greater than 50 micra and said metallic component has a grain size ranging between 10 and 150 micra.

13. The composition of claim 1 in which said silicide is composed of 45% silicon and 55% molybdenum and has a grain size less than 10 micra and said metallic component is composed of aluminum with finer grains than 325 United States mesh, said silicide constituting 97% of said mixture of components and said aluminum constituting substantially the balance thereof, said mixture of components being admixed into a carrier medium destructible at flame coating temperatures.

14. The composition of claim 13 in which said medium comprises polyethylene and is extruded to form a string suitable for flame spraying equipment.

15. A composition for flame spraying as defined in claim 1, wherein said composition is in sintered and pulverized form.

16. A process for flame spraying on a surface a coating largely comprising a silicide of molybdenum, said process including flame spraying on said surface a composition including a refractory component comprising at least one compound selected from the group consisting of refractory silicon compounds of the transition metals of the fourth, fifth and sixth groups of the periodic table and carbon, said refractory component at least largely comprising a silicide of molybdenum and being in the form of powder particles which when exposed to the atmosphere automatically form thereon coating films of silicon dioxide interfering with their adhesion together, said composition further including a metallic component in the form of powder particles of a metal having a strongly positive heat of reaction with oxygen as compared to that of silicon, said components being intermixed and said composition being heated to temperatures at least softening said silicide during said flame spraying and said metal being effective at said temperatures to reduce said silicon dioxide films and expose clean surfaces on said refractory component particles which adhere together on said surface, said composition being heated during said flame spraying by means adding to the heat of reaction produced by said reduction of said films as required to maintain said reaction and said temperatures.

17. The process of claim 16 in which said components are admixed with a heat destructible carrier medium facilitating their handling by flame spray equipment, said medium being destroyed by the heating to said temperatures.

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Patented Aug. 14, 1962

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PROCESS FOR APPLYING TUNGSTEN CARBIDE PARTICLES TO A WORKPIECE SURFACE

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No Drawing. Filed Aug. 19, 1957, Ser. No. 679,052
4 Claims. (Cl. 117—22)

This invention relates to a process for applying tungsten carbide particles to a workpiece surface.

It is a conventional process to hard surface various types of cutting or wearing surfaces by means of welding tungsten carbide particles to the surface. The conventional process normally consists of heating tungsten carbide to above the 3000° C. melting point of the tungsten carbide and then casting the molten material into shot, which is then crushed into tiny particles ranging from 12 mesh to 100 mesh. Thereafter, these tiny particles are welded to the workpiece surface by the use of conventional welding torches or the like.

The disadvantage with the conventional process is that a large part ofthe tungsten carbide material is lost by vaporization, oxidation or dissolution during the welding process to form compositions of iron and tungsten carbide which do not have the hardness or abrasion resistance of the original tungsten carbide particle. Also, where a workpiece is formed of a ferrous material, the ferrous material acts as a dissolving agent for the tungsten carbide so that a great part of the tungsten carbide is dissolved into the molten ferrous material during the welding process at the point where the heat is applied. Thus, only a very small part of the original tungsten carbide actually remains on the surface of the workpiece to form the hard coating which is desired. Since the price of tungsten carbide is extremely high, the loss of this material is an extremely expensive loss.

Attempts have also been made to braze tungsten carbide particles to a workpiece surface, but these attempts have, for the most part been unsuccessful because the tungsten carbide is not readily wettable and thus, the brazing material will not adhere to the particles.

Thus, it is an object of this invention to apply particles of tungsten carbide to a workpiece surface to thereby provide a hard surface, but in so doing, to prevent the loss of tungsten carbide entirely or to hold this loss to an absolute minium so that for all practical purposes there is no loss.

In addition, it is an object of this invention to treat the tungsten carbide particles by surface coating them with nickel or nickel-nickel phosphide so that they become wettable and may be welded or brazed to a workpiece surface.

These objectives are achieved by completely coating the tungsten carbide particles with nickel or with nickel-nickel phosphide. This coating acts as a sacrificial material which evaporates, oxidizes, and also dissolves in iron. Thus, in application of the particles to a workpiece there is almost no loss of tungsten carbide. Likewise, the coated tungsten carbide particles are wettable and in the case of nickel-nickel phosphide, self-fluxing to some extent whereby they may be easily brazed to a workpiece.

Another object of this invention is to form particles of tungsten carbide, suitable for use in hard surfacing workpieces, by crushing pieces of cemented tungsten carbide raw material and then surface coating the particles with nickel as mentioned above. The crushed particles normally consist of a number of tiny particles of tungsten carbide, each somewhere in the order of 2 to 12 microns in size, cemented together by approximately 5% to 25% by weight of cobalt. The large pieces of cemented tungsten carbide may be crushed mechanically into small size particles in the approximate range of ¼ inch to minus 325 mesh as will be explained below.

These and other objects of this invention will become apparent upon reading the following description:

Forming the Nickel Coated Tungsten Carbide Particles

The raw material particles for this process may consist of either pieces of tungsten carbide or large pieces or chunks of cemented tungsten carbide. Where the first is used, the tungsten carbide is heated to above its melting point of approximately 3000° C. and then cast into pieces which are subsequently crushed into tiny particles which may range in size from ¼ inch to minus 325 mesh. This is a conventional process of forming these tiny particles. The preferred raw material, however, is cemented tungsten carbide which consists of large pieces of tungsten carbide containing tiny particles of approximately 2 to 12 micron size pieces of tungsten carbide cemented together by approximately 5 to 25%, by weight, of cobalt. These cemented pieces are crushed into the desired mesh size ranging from approximately ¼ inch to approximately minus 325 mesh and are then used as the raw material.

The raw material particles are then completely coated with nickel or nickel-nickel phosphide. The nickel coating can be obtained by dipping the particles in an electrolytic bath containing nickel arranged to deposit a substantially pure nickel plating on the outside surfaces of each of the particles. In the alternative, the particles can be nickel plated by the use of the chemical process described in the patent to Brenner et al., No. 2,532,283 of December 5, 1950. Where the chemical process is used, the coating is in the form of a nickel phosphorus alloy which contains nickel phosphide; the coating containing approximately 5 to 14% phosphorus, by weight.

In each of the coating methods, the tungsten carbide particles are completely coated with a very thin coating of nickel. The thickness of the coating is not particularly critical, but the surfaces should be as completely coated as possible. Thus, the time for dipping the particles in the electrolytic bath coating will be simply that length of time necessary to form a complete coating, regardless of thickness of coating.

Hard Surfacing of Workpieces by Welding

The nickel coated tungsten carbide particles may then be applied to a workpiece by means of placing a number of the particles upon the surface of the workpiece and heating the particles and the workpiece surface with a conventional welding torch. The heat of welding which is quite high and would probably exceed the 3000° C. melting point of the tungsten carbide and thereby cause evaporation and oxidation or solution of the tungsten carbide instead causes the nickel coating to fuse with the workpiece surface and it is the nickel coating which either evaporates or oxidizes or in the case of a ferrous workpiece, dissolves so that the tungsten carbide remains to form a hard surface. With this process there is little or no loss of tungsten carbide and since this tungsten carbide material is quite expensive, there is a large cost saving.

Hard Surfacing by Flame Spraying

Alternatively, the particles may be applied to a workpiece surface by spraying fine particles, somewhere in the range of approximately minus 150 mesh size, onto the workpiece and simultaneously flame heating the workpiece and particles. The flame spraying process of applying particles to a workpiece is known in the art. Where tungsten carbide particles are used, most of the particles do not stick to the workpiece but rather bounce off during the spraying process. What few particles do stick

are further depleted by the loss due to oxidation, dissolution, and evaporation. However, by nickel coating the particles as herein described, the nickel coating, being melted by the heat as the particles travel towards the workpiece, cements the particle to the workpiece and any loss of material is sustained by the coating rather than by the expensive tungsten carbide. In some applications, a small amount of Colmonoy No. 6 (a nickel-silicon-boron alloy) made by the Colmonoy Company may be added to the particles to further act as an adhesive agent. This hard brazing material has a low melting point and a wide plastic range and thus increases the adhesion of the particles to the workpiece. The amount of Colmonoy No. 6 added, if any is desired for any particular application, depends upon the speed of flame spraying, the heat, the material of the workpiece, etc., and may be determined by test.

Hard Surfacing by Brazing

Alternatively, the nickel coated tungsten carbide particles may be applied to the workpiece surface by means of a brazing process. This can be accomplished by mixing the particles with a brazing powder in a dry unheated state and then brazing in the conventional way by applying the powder mixture to the surface of the workpiece then passing the workpiece through a brazing oven or the like, which is hot enough to melt the brazing material and cause it to fuse to the workpiece. The temperature and time required varies with the particular brazing material used and is determined by test.

Normally, tungsten carbide particles cannot be brazed to a workpiece because the tungsten carbide is not readily wettable by the brazing material. However, when the particles are nickel coated as herein disclosed, the nickel coating is wettable and thus, the nickel coated particle can be easily handled and brazed to a workpiece surface.

One sample brazing material which has been found suitable for this purpose is Allstate No. 13 made by the Allstate Company, which is a nickel bronze brazing powder or rod. Obviously, many other types of brazing material would operate for the purpose described. It is to be understood, that the brazing problem here is that of brazing nickel to the workpiece rather than tungsten carbide to the workpiece because the particles are coated with nickel and therefore any brazing material which would serve in brazing nickel to a workpiece would operate here.

Hard Surfacing With a Diamond Matrix

It is also contemplated to hard surface a workpiece by mixing the nickel coated tungsten carbide particles with diamond particles, plus a binder such as bronze or monel or iron or iron plus Colmonoy No. 6. The combination of the tungsten carbide and the diamond forms an excellent grinding wheel surface and also is excellent as a surface for core bits for oil well drilling, etc.

Advantages

As mentioned, the problems in using tungsten carbide are that the tungsten carbide is not readily wettable, and also, that there is a loss of tungsten carbide due to evaporation, oxidation, and dissolution in ferrous workpiece surfaces.

Nickel coating the tungsten carbide substantially eliminates the loss of the tungsten carbide mentioned above, as well as forms a wettable surface on the tungsten carbide particles. Thus, the particles may be easily used in the normal welding process or in the ordinary brazing processes to form a hard surface on a workpiece.

Where the particles are used in a brazing process, the phosphorus contained in the nickel-nickel phosphide coating on the particles acts as a flux so that the material is almost completely self-fluxing. Thus, the phosphorus reduces the melting point and since the particles contain approximately 5 to 14% phosphorus with the nickel in the chemical process type of coating, only a small amount of extra flux is required. For example, where phosphorus type fluxes are used, approximately 12% by weight is necessary with approximately 88% nickel to form a good self-fluxing brazing alloy. Since the particle coating already contains 12% phosphorus or close to 12% only a small amount of additional flux is needed.

This invention may be further developed within the scope of the following attached claims and accordingly, it is desired that the foregoing description be read as being an operative embodiment of this invention and not in a limiting sense.

I claim:

1. A process of applying tungsten carbide particles to a ferrous metal surface to impart thereto hard wearing and cutting properties comprising crushing the tungsten carbide to a particle size in the range of ¼ inch to 325 mesh, coating the particles with a thin continuous film of metallic nickel, and then applying the said particles to the ferrous metal surface with sufficient heat to fuse the nickel coating to the ferrous metal, thereby binding the particles to the surface.

2. The method of applying cemented tungsten carbide, having cobalt metal as the cementing matrix, to a ferrous metal surface to impart thereto hard wearing and cutting properties comprising first crushing the cemented tungsten carbide to a particle size in the range of ¼ inch to 325 mesh, coating the crushed cemented tungsten carbide particles with a thin continuous film of metallic nickel, and then applying the said particles to the ferrous metal surface with sufficient heat to fuse the nickel coating to the ferrous metal, thereby binding the particles to the surface.

3. The method as defined in claim 1 wherein the nickel coating upon the particles contains about 5 to 14 percent phosphorus.

4. The method as defined in claim 1 wherein the nickel coated tungsten carbide particles are further mixed with a low melting point hard brazing material before being applied to said ferrous metal surface.

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ACKNOWLEDGMENT

This investigation was promoted by a grant for fundamental scientific research from the Ministry of Education of Japan and also a grant from Nippon (Japan) Carbide Industries Inc., for which the authors wish to express their deep appreciation.

Manuscript received November [illegible]. This paper was prepared for delivery before the [illegible]gh Meeting, October 9-12, 1955.

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Structure of Chemically Deposited Nickel

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ABSTRACT

An analysis was made of the structure of the Ni deposit produced by the catalytic Ni reduction process. X-ray and electron diffraction revealed that the Ni deposit was an amorphous solid. The structure appeared to be unrelated to and independent of the nature of the substrate and thickness of the deposit.

Metallographic examination revealed a dense material, free of voids, and perfect conformity to the substrate surface profile. Etching produced a lamellar structure the variation in etching intensity being interpreted as variations in dissolved P. In platings, the lamellae lay parallel to the plane of the substrate. Growth faults were observed traversing the thickness dimension from substrate surface irregularities. The amorphous structure reverted to a crystalline phase mixture of Ni and Ni_3P at low temperatures with a large heat evolution.

Basic reactions of chemical Ni *coating processes.*—The Kanigen[1] Ni plating process is based on catalytic reduction of Ni ions in the presence of hypophosphite ions.

The hypophosphite anion in aqueous medium is oxidized to the phosphite ion with evolution of H, the rate being a function of temperature and hypophosphite concentration. This oxidation takes place spontaneously (homogeneous reaction) in alkaline solution at elevated temperature, while, under neutral or moderately acid conditions, the presence of a catalytic metal belonging to Group VIII of the periodic system, particularly Pd or Ni, is required (catalytic heterogeneous reaction). Wieland and Winkler (1) assumed, on the basis of organic analogies, a catalytic de-hydrogenation of the hypophosphite molecule according to the equation:

$$H(H_2PO_2) \xrightarrow[\text{Catalyst}]{-2H} HPO_2 + H_2O \longrightarrow H_3(HPO_3)$$

Hypophosphorous acid — Metaphosphorous acid — Orthophosphorous acid

In a study of the mechanism of catalytic hypophosphite oxidation, Franke and Moench (2), using D as a tracer in lieu of H atoms, confirmed Wieland's hypothesis and demonstrated that hypophosphite did not actually "decompose" the water molecule.

If the aqueous alkaline hypophosphite solution is relatively concentrated and contains cations of heavy metals which can be reduced, such as Ni, Co, Cu, Bi, Ag, Pd, Au, etc., a dark spongy or lustrous precipitate of

[1] Kanigen is a trade name used by General American Transportation Corp. and its licensees to identify the Ni deposit or coating which is the product of a catalytic Ni reduction process.

E 870

when the solution is heated. In the case of Ni and Co, solid metal-phosphorus alloys are formed.

Furthermore, if the metal cation present in the neutral or slightly acid hypophosphite solution is that of a catalytic metal such as Ni, and a catalytic solid surface is immersed simultaneously, deposition will be limited to said surface and will continue until the solution is depleted of hypophosphite ion or of the metallic cation. The gross equation was written by Brenner and Riddell (3):

$$NiCl_2 + NaH_2PO_2 + H_2O \xrightarrow{\text{Catalyst}} Ni + NaH_2PO_3 + 2HCl \quad \text{(II)}$$

The reduction of Ni ions appears to be caused by atomic (nascent) H adsorbed as a condensed layer on the catalytic surface. Concurrently, there is a secondary reaction among the hypophosphite (and probably the phosphite) ions, atomic H, and Ni cations, resulting in the formation of Ni phosphide (possibly with a phosphonium salt as intermediate compound).

The basic reactions can be expressed tentatively by the following:

$$n(H_2PO_2)^- \xrightarrow{-2nH \text{ Catalyst}} n(PO_2)^- \quad \text{(III)}$$

$$2H^+ \rightarrow H_2 \quad \text{(IV)}$$

$$(PO_2)^- + H_2O \rightarrow H(HPO_3)^- \quad \text{(V)}$$

$$Ni^{++} + 2H \xrightarrow{\text{Catalyst}} Ni^\circ + 2H^+ \quad \text{(VI)}$$

$$H_2PO_2)^- + 3Ni^{++} + 7H \xrightarrow{\text{Catalyst}} Ni_3P + 5H^+ + 2H_2O \quad \text{(VII)}$$

From the catalytic surface of the solid, a stream of H bubbles escapes, and deposition of a high Ni-low P alloy takes place. This alloy is itself a catalyst, so that the coating thickness will grow constantly for a certain time period, which is limited by the *p*H decrease and instantaneous ion concentration. As can be seen from Eq. (VI) and (VII), the *p*H of the bath will drop as the reaction proceeds.

General American processes.—The character of the basic reaction and the drawbacks of the Bureau of Standards method, including published modifications thereof, indicated the direction research and development work should take for industrial production.

The principal disadvantages of the original Bureau of Standards process (3) are: slow rate of deposition, lack of stability of the bath in continuous operation, dull and even rough plating when the bath is used for longer periods, nonhomogeneous deposits in the vertical direction, and relatively high cost (mainly because of a short useful life of the coating solution).

Study of a simple acid bath containing Ni and hypophosphite ions and a buffer such as sodium acetate revealed that in order to obtain both maximum deposition rates and optimum plating quality, reagent concentrations, ion ratios, and initial *p*H are critical (4).

It was discovered that the addition of short-chain aliphatic dicarboxylic acids and/or soluble fluorides ("exaltants") will substantially raise the coating rate (5, 6).

If a chemical coating bath is to be used in a production plant, it is very important to increase the span of its useful life. The limit of phosphite concentration, at which nickel phosphite precipitates, can be raised from 0.07 to about 1.0 mole/l by judicious addition of certain Ni chelating compounds, provided an "exaltant" is present to keep the deposition rate at a practical level.

The problem of bath stability is among the most serious in an industrial plant. The first visible result of excessive bath lability is the appearance of foam (due to excess H) and finely dispersed "black precipitate" (Ni-P alloy), which, because of its enormous area, acts as a very large catalytic surface. It was found that certain inhibitors, if used in properly adjusted amounts, act selectively (mainly because of geometric factors) on the suspensoids (active nuclei) making them noncatalytic, while they reduce only very slightly the rate of Ni-P deposition on the solid body to be coated.

In addition to the above improvements in bath composition, which are essential for industrial production, new principles were established relating to continuous operation and plant design, based on the requirements of catalytic reduction (7), as follows: (*A*) Because the plating rate is an exponential function of temperature, the highest possible operating temperature (below the boiling point of the solution) is desirable in order to obtain maximum speed of deposition. (*B*) It is necessary to feed continuously the consumable reagents (Ni, hypophosphite, hydroxyl ions, and stabilizer) in order to maintain maximum coating rate, optimum quality, and have the coating composition constant in a direction perpendicular to the catalytic surface. The regeneration chemicals can be added as concentrated solutions or powdered solids (to avoid bath dilution) if the bath is first cooled to a relatively low temperature (8, 9) (to prevent bath decomposition). (*C*) It is possible to meter the regeneration chemicals controlled by *p*H measurements because the various reactions in the bath are interrelated [see Eq. (III)–(VI)], and there is a fixed proportionality between the quantity of hydroxyl ions required to keep the *p*H constant, the weight of Ni-P deposited, and the amount of hypophosphite consumed.

The requirements stated above have been incorporated into the industrial Kanigen coating system, which can be described schematically as follows (7, 8, 10). The bath is prepared and kept at a relatively low temperature of about 130°F. It flows into the coating tank through a heat exchanger, which raises its temperature to 208°–210°F. From the coating tank it is pumped into a regeneration vessel where reagents are added in controlled amounts to bring the solution's components back to their original concentration. The liquor then flows through a filter and circulates back through the heater to the coating tank.

The plant is designed in such a manner that most of the handling (pumping, filtration, etc.) of the bath is done in the "cold" section.

In many cases, when the interior of a large vessel is to be coated, the part itself becomes the plating tank.

The bath may be used until such time as the concentration of phosphite ions builds up to the point where nickel phosphite begins to precipitate. A procedure has been developed (patent pending), with several improvements

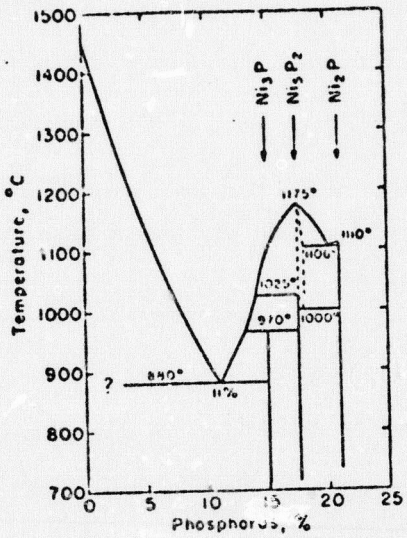

FIG. 1. Constitution of the system Ni-P

under study, which allows removal of phosphites and reclamation of the used bath without introducing any foreign ions.

Pretreatment of parts for coating by chemical reduction is essentially the same as for electrolytic plating. Because no electrical equipment is needed in a chemical coating plant, soak-cleaning procedures are preferred. Some special techniques had to be developed or adapted for deposition of Ni on certain noncatalytic metals, alloys, and nonmetals.

Composition and Constitution

The chemically reduced metal coating was primarily metallic Ni containing 7–10 w/o P. Analyses were conducted for both metallic and nonmetallic impurities. The material used for this purpose was a quantity of deposited foil about 10 mils thick which had been stripped from panels specially treated to permit easy stripping. The foil was bright, smooth, and apparently free of surface imperfections.

Spectrographic analysis for heavier elements showed only trace amounts of Al, Ca, Fe, Mg, Pb, and Si. The term "trace" is a qualitative definition for less than 0.1% and probably less than 0.01%. Analyses for what are normally considered interstitial elements yielded the following results: C, 0.04%; O, 0.0023%, N, 0.0005%, H, 0.0016%.

The form of the phase diagram was originally mapped out by Konstantinov (11) in 1908; no work has been reported since. His version of the diagram is shown in Fig. 1. There is no information on the solid solubility of P in Ni, although from considerations of size factor and relative electro-negativity, it might be expected to be of the order of 5 w/o.

The low melting eutectic is a phase mixture of Ni solid solution and Ni_3P. The structure of the Ni_3P phase was reported by Nowotny and Henglein (12) as tetragonal: $a = 8.93$Å; $c = 4.39$Å; $c/a = 0.49$.

X-ray Studies on the Ni Coating

Investigations on the structure of the Ni deposit were carried out by Debye-Scherrer photographs of surface scrapings, Geiger counter tracings of surface reflections of the platings, transmission photographs of stripped films, and low-angle-scattering photographs of ground chips.

The Ni coatings showed the structure of an amorphous solid substance with "liquid-like" disorder of the atoms. Different base materials (such as Al, brass, steel, and Bakelite) and different pretreatments of Al base plates had no appreciable influence on the structure of the platings. The deposition of different thicknesses (1–30 mils) on these base materials had no influence on the amorphous structure of the coating.

The unique character of this physical state justifies a short discussion of amorphous solids and the experimental evidence for describing chemically reduced Ni plating as a liquid-like amorphous solid. The term "amorphous" is often used to describe structural forms for which more specific terms can now be given. In some deposits and dehydration products, a chaotic state of aggregation can be detected (13), e.g., small molecular groups loosely bound together in a quite irregular way show a high percentage of free space. The diffracted x-ray intensity of this gas-type, chaotic state extends continuously from the direct beam as in the case of diffraction of gases. The intensity of the scattered radiation in the vicinity of the central beam depends on the difference in scattering power or electron density between the two phases of the porous system. Other examples which show gas-type scattering are amorphous SiO_2, amorphous Al_2O_3, and highly dispersed carbon black (14).

With colloidal crystallites, the somewhat broadened central beam and the broadened diffraction lines are separated by distinct minima in the intensity of the scattered radiation. When the amorphous or crystalized particles are squeezed close together, the interstices are small compared with the particle size; the resultant intensity of the low-angle scattering is considerably decreased. All dense systems produce a weak, low-angle scattering, and this phenomenon can be used for analysis of the internal structure of the amorphous Ni.

A low-angle scattering x-ray photograph of ground chemically reduced Ni showed the very small scattering effect of a dense substance. This was probably not caused by pores between the amorphous aggregates but by the microlayer structure shown in the section on metallography and representing pseudo variations in P content.

In ordinary liquids, a clear intensity minimum separates the direct beam which is not broadened from the first diffraction band, i.e., the liquid halo. The x-ray patterns are characterized by a few wide bands, generally less than three (15). Distances which frequently occur between the atoms or molecules of the amorphous solid correspond to each halo on the diffraction pattern.

The x-ray powder patterns of chemically reduced Ni and the Geiger counter tracings of plated surfaces showed only one diffuse ring with a "d" spacing of 2.01Å. The occurrence of only one ring together with the extremely

small low angle scattering characterize chemically reduced Ni deposits as liquid-like, dense, amorphous solids.

In the x-ray diagrams of liquids and liquid-like substances, the position of the peak intensity of the first halo corresponds approximately to the first strong line of the crystallized modification of the same substance. Closer investigation of the peaks of the x-ray patterns have shown, however, that in some cases the peaks do not coincide with the position of the strongest reflection of the crystallized compound. X-ray diagrams of vitreous silica, amorphous Se (obtained by quenching from a melt), and amorphous explosive Sb are examples of liquid-like amorphous solids with shifts in the positions of the halo (14, 16).

A visual inspection of the x-ray diagrams of amorphous and crystallized (heat treated at 430°C) Ni seemed to indicate that a similar shift of the position of the halo occurred with amorphous Ni. The sharp line of (111) reflections from crystalline Ni lay on the inner side of the halo. Because of the breadth of the halo and its diffuseness, a quantitative estimate of the shift was difficult.

Ring or line broadening could also have been caused by a very small crystalline particle size, but the broadening would have been symmetrical about the sharp line position. Furthermore, use of an approximate estimate of the halo breadth and the Scherrer formula for line broadening yielded the ridiculous answer of a mean particle size of a few atomic distance dimension. Electron diffraction patterns of 15 different chemically reduced Ni deposits plated under a wide variety of different conditions and in different thicknesses confirmed the amorphous character of at least the surface layers.

The density of amorphous Ni was determined in a pycnometer at 20°C and found to be $D_{20°} = 7.85$ g/cc.

The powder pattern of amorphous Ni heated in N for 1½ hr at 430°C showed a sharp line sequence of two structures. The Ni lines were easily distinguished. The remaining lines indexed provisionally on a tetragonal lattice of parameters $a = 9.01$Å and $c = 4.42$Å which is reasonably similar to the structure of Ni_3P proposed by Nowotny and Henglein (2).

A Metallographic Study of Chemically Reduced Ni

Preparation of specimens for optical metallography.—The first important phase of preparation was cutting and mounting specimens. The as-deposited coating was brittle, and simple cutting of a plated specimen with a hack saw tended to crack and flake off the deposit. It was convenient to electroplate the specimen with a heavy deposit of Ni to provide some support for the coating. The choice of Ni as a backing material was based on mechanical properties and final etching characteristics. Probably Cr would be too brittle to provide suitable support, and Cu would induce undesirable staining during etching. There was no difficulty in distinguishing the electroplated Ni from the chemically reduced Ni in polished and etched specimens.

Metallographic specimens are normally mounted in a thermosetting Bakelite under several thousand psi pressure. This method tended to promote formation of cracks in the plate, the so-called "dikes" observed by others

Fig. 2. (*Left*) Microstructure of 10 mil chemically reduced Ni on steel (etched). Fig. 3. (*Right*) Microstructure of 10 mil chemically reduced Ni on steel (unetched).

(Fig. 2 and 3). The etched structure revealed dark bands traversing the deposit from the substrate interface to the surface. On removal of the etch by repolishing, the dark band was more clearly resolved as a true crack.

It was possible to avoid the occurrence of cracks (which are artifacts) by mounting specimens in a room-temperature-setting compound, Epon, manufactured by the Shell Oil Company. This medium was mixed prior to casting with 8–10% by weight of triethylene tetramine which acts as a polymerizer. During curing the temperature remained below 50°C and no pressure was applied. The specimen was placed inside a polyethylene ring, approximately ½ in. high, 1 in. OD, and $\frac{1}{16}$ in. thick, which rested on a thin sheet of polyethylene film. The mixed resin was poured into the mold thus formed and allowed to solidify. Mounts thus prepared were ready for polishing in 3 hr.

Specimens for microexamination were processed as follows: (*a*) rough grind on a belt sander to create a flat surface, (*b*) rough lap on a cast iron lapping wheel with oil-suspended Carborundum abrasive, (*c*) rough polish (kerosene suspension of diamond powder), and (*d*) fine polish (water suspension of Linde "B" sapphire powder).

Routine etching reagents recommended for Ni alloys were unsuitable for revealing the structure of as-deposited chemically reduced Ni. An electrolytic etch was developed in which an electrolyte of 10% chromic acid in water was used. A cell potential of 2 v applied for about 5 sec was usually sufficient. Both cast chemically reduced Ni and heat-treated metal reacted satisfactorily to the standard $FeCl_3$-HCl etchant used for Ni alloys.

Analysis of the structure of chemically reduced Ni coatings by optical metallography.—Most of the studies were conducted on 10 mil plates on steel panels. On occasion it was easier to reveal the detail of basic structures on lump specimens of tank deposits.

In the unetched condition, platings at 1000 diameters magnification were completely sound and showed no porosity, channels, or other types of voids. The plate followed the fine contour of the substrate surface in amazing detail. A number of the photomicrographs show burrs and other asperities with re-entrant angles. In all instances, the Ni deposited so completely that there were no observable voids between plating and substrate.

Fig. 4 and 5 illustrate some of the essential structural characteristics of chemically reduced Ni coatings. The structures reveal a peculiar array of parallel or concentric

E 873

FIG. 4. (*Left*) Microstructure of tank deposited chemically reduced Ni in cross section. FIG. 5. (*Right*) Microstructure of tank deposited chemically reduced Ni in cross section.

FIG. 6. (*Left*) Microstructure of 10 mil chemically reduced Ni on steel (as deposited). FIG. 7. (*Right*) Microstructure of a piece of tank deposited chemically reduced Ni after heat treatment at 700°C for 1 hr.

striations. These striations are characteristic of periodic variations of composition (presumably P) rather than alternate lamellae of different phases. Growth appears to originate at point centers or nuclei and develops at an equal rate in all directions, hence, the concentric circle pattern. When the two growth colonies meet, they generate a matching interface or fault. There is no evidence optically that the match at the fault is less than complete. If it were not true that x-ray diffraction patterns indicate an amorphous structure, these faults would come under the normal designation of grain boundaries. But since a grain boundary connotes an interface between two unique adjoining crystallographic orientations, the term cannot be properly used in this instance. It does appear, however, that the atomic disregistry at the fault is of the same degree as is thought to exist at a grain boundary, although this must be regarded only as reasonable conjecture.

On thin platings of the order of 10 mils and less, the population of surface nuclei is apparently so high that the spherical growth fronts join as a common "wave" front almost immediately, and the resultant structure shows the laminations as parallel (Fig. 6).

Evidence that the striations in the as-deposited chemically reduced Ni reflect variations in P content may be observed in microstructures of heat-treated deposits. By heat treatment the metastable as-deposited state reverts to the equilibrium phase mixture of Ni solid solution (containing very little P) and the intermetallic compound Ni_3P. The population of Ni_3P particles may be used as an indication of the original P content. Fig. 7 shows the appearance of one of the original striations after heat

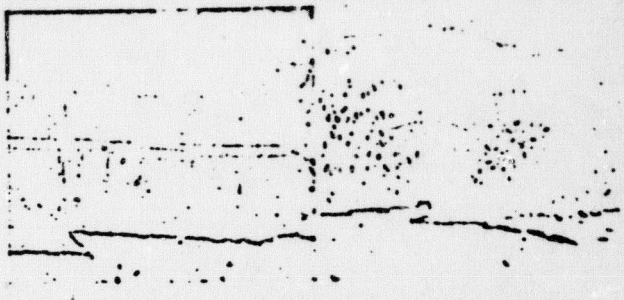

FIG. 8. (*Left*) Microstructure of 10 mil chemically reduced Ni on steel illustrating the effect of surface irregularities on the occurrence of growth faults in the deposit. FIG. 9. (*Right*) Microstructure of 10 mil chemically reduced Ni on steel illustrating the effect of surface irregularities on the occurrence of growth faults in the deposit.

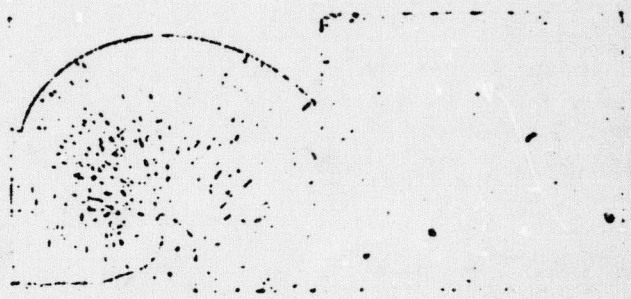

FIG. 10. (*Left*) Microstructure of 10 mil chemically reduced Ni on steel illustrating the growth of chemically reduced Ni around the burr of a sheared edge. FIG. 11. (*Right*) Structure of as-cast chemically reduced Ni—primary dendrites of Ni in a eutectic of Ni and Ni-P.

treatment, and it can be seen that the number of Ni P particles within the striation is less than on either side of it.

All the as-deposited coatings (Fig. 4 and 6) showed a series of secondary striations radiating from individual nucleus points or the surface. These secondary striations were discontinuous in pattern, and appeared only on etching. Therefore, they reflected some variation in chemical content. There was no vestige of them after heat treatment. Their nature could not be deduced from studies so far pursued.

Three microstructures are presented to illustrate the influence of surface imperfections on the structure of deposits on steel panels. Fig. 8 and 9 show the occurrence of burrs left on the steel by machining. In each instance growth faults originate from the surface irregularities. A particularly detailed picture of structures and growth faulting is illustrated in Fig. 10 at a sheared edge of a steel panel.

Fig. 8 is particularly important to the general theory of the deposition process. In the first set of parallel striations in the deposit, the displacement in adjoining growth areas is the same as the original displacement of the two surface levels on the steel. This indicates that growth rates are identical everywhere in the immediate vicinity, and that modifications in the reaction kinetics which develop different P content deposits occur at the same time over the surface, irrespective of their projection into the solution.

Transformation Characteristics of Chemically Deposited Ni

Nature of transformations.—Since it was concluded that the as-deposited Ni may be interpreted as a liquid-like structure in which the primary alloy element, P, is randomly distributed on an atomic scale, the structure is metastable, both with respect to crystallinity and with respect to an equilibrium phase mixture of Ni solid solution and a Ni-P intermetallic phase, Ni_3P.

The ultimate equilibrium state was easily developed by melting a lump of chemically reduced Ni originally deposited on tank walls. The microstructure illustrated in Fig. 11 shows primary dendrites of Ni solid solution and a fine but resolvable eutectic of Ni and an intermetallic compound. The actual configuration seen in Fig. 11 is characteristic of the solidification process, but the products of crystallization are identical to what must ultimately derive from heat treatment of chemically reduced Ni below its melting point. X-ray diffraction powder patterns of the cast material gave a sharp pattern from which lines of the Ni structure could be easily distinguished from those of the intermetallic compound.

Metallography of heat treated chemically reduced Ni.—Fig. 12 and 13 illustrate structural configurations developed at two temperatures of heat treatment. In each case the transformation proceeded to equilibrium as revealed by x-ray diffraction patterns. The transformation to equilibrium produced a dispersion of Ni_3P in a Ni matrix. Clearly, the size of the Ni_3P particles was temperature dependent, i.e., the lower the heat treatment temperature, the finer the dispersion. The structure of a specimen annealed for 1 hr at 400°C was so fine that the particles cannot be individually resolved.

Generally, it may be inferred from such a sequence of microstructures that the finer the dispersion, the harder the structure. This is shown by hardness tests which show a progressive decline in the hardnesses of structures annealed at 400°, 500°, 600°, 700°, and 800°C. Hardnesses for these temperatures (1 hr anneal) were 1195, 980, 739, 605, and 544 VHN, respectively. Furthermore, it may be inferred that if some ductility can be induced in this material, it will be by annealing at 800°C or as close to the melting point as possible.

Kinetics of transformation.—It was found by experiment that hardness can serve as a tool for following time dependence of the state of transformation. Coupons were cut from a steel panel plated with a 10 mil deposit of chemically reduced Ni. The coupons were then annealed for specific times at 200°, 300°, or 400°C. Vickers hardness measurements were taken of the heat-treated Ni in the plane of cross section after cold mounting and polishing. A microhardness tester is mandatory for this type of work. In this instance, a Leitz instrument with a 100 g load was used. Reported hardnesses are averages of 5–10 measurements.

Trends of hardness vs. time for three temperatures are shown in Fig. 14. At 400°C a hardness peak is reached in about 10 min. Actually, in x-ray diffraction patterns the amorphous halo disappears after only 1 min at temperature and only the sharp lines of Ni and Ni_3P appear. There is a question then of why hardness continues to increase after 1 min. It may be that transformation proceeds by two successive processes: a reversion from undercooled liquid solution to a supersaturated crystalline solution, then a rejection of Ni_3P from the crystalline supersaturated solid solution. There are differences in relative intensities of lines and in the occurrence of certain lines in patterns taken after 1 min and after 60 min of heat treatment. Whatever the processes involved, the times are so brief that control short of complete transformation would be impractical.

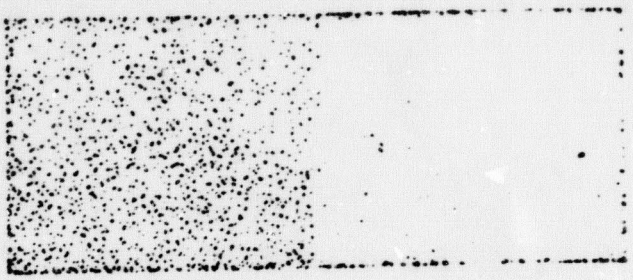

Fig. 12. (*Left*) Structure of chemically reduced Ni after heat treatment for 1 hr at 800°; dispersions of Ni_3P in a matrix of Ni. Fig. 13. (*Right*) Structure of chemically reduced Ni after heat treatment for 1 hr at 600°C; dispersions of Ni_3P in a matrix of Ni.

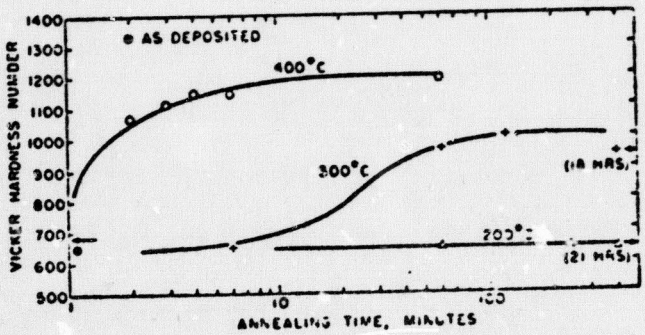

Fig. 14. Hardness of chemically reduced Ni vs. time and temperature of heat treatment.

At 200°C, even after 21 hr of heat treatment, there was no measurable change in hardness. X-ray patterns also showed the same amorphous halo observed in the as-deposited state. Accordingly, it may be concluded that no transformations occur at 200°C, at least none within 21 hr.

The 300°C anneal, as expected, followed a trend of slow transformation. Hardness continuously increased over a 2-hr period. As at 400°C, the amorphous structure, although it persisted for at least 5 min at temperature, disappeared long before the hardness reached a peak value.

Thermal evolution during heat treatment of chemically reduced Ni.—One of the main questions regarding the nature of the as-deposited metal is whether the structure is that of an undercooled liquid or of a submicroscopically fine-grained supersaturated solid solution. If the particle size of crystalline aggregates is small enough, the line broadening conceivably could approach the magnitude customarily found with undercooled liquids. One of the methods for distinguishing between these alternatives is through a study of x-ray low-angle-scattering and x-ray diffraction characteristics which are discussed in another section of this paper.

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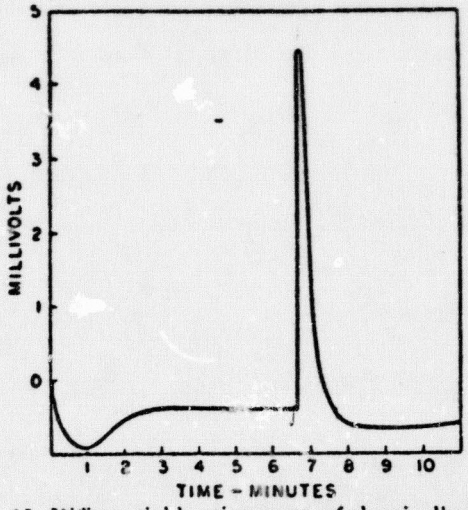

FIG. 15. Differential heating curve of chemically reduced Ni.

A second method which can give a qualitative indication is some measure of the magnitude of thermal evolution accompanying the transformation of the as-deposited metal to the equilibrium phase mixture of Ni and Ni_3P. Invariably, latent heats of fusion are substantially larger than latent heats of crystalline state transformations. For instance, the latent heat of fusion of Fe is 3700 cal/g-mole, whereas the heat of transition from $\alpha \rightarrow \gamma$ Fe is only 210 cal/g-mole; under adiabatic conditions these would correspond to temperature rises of 330° and 21°C, respectively. A survey of available data on latent heats of transformation indicates that they are all less than 1000 cal/g-atom and usually much less. Such thermal evolutions should then incur ideal temperature rises of less than 100°C, but since an ideal adiabatic system is very difficult to attain, the temperature rises should actually be considerably less.

A simple experiment was devised to study thermal evolution effects in chemically reduced Ni. Two pieces of Ni tank deposit in the form of plates about 0.020 in. thick and 1 cm^2 area were chipped to size. One piece was heat treated in advance so that no further transformations would occur. A fine wire chromel-alumel thermocouple was spot welded to each of the pieces and connected in opposition to a Speedomax high-speed recording potentiometer. Each of the pieces of chemically reduced Ni was set in a test tube for convenience of handling, and the assembly was immersed in a lead bath.

Since both pieces were heated at about the same rate, differential potential remained about zero. At 400°C, as recorded by an auxiliary thermocouple, there was a sharp rise in differential potential which lasted for about 1½ min and then disappeared. A reproduction of this portion of the record is shown in Fig. 15. The burst of differential potential verified that the chemically reduced Ni liberated a substantial amount of heat on transformation to its equilibrium state. Furthermore, it is obvious that the transformation rate at 400°C is extremely rapid.

The maximum differential potential was 5 mv, which corresponds to a temperature rise during transformation of 122°C. Since the conditions of testing were far from adiabatic, this corresponded to a thermal evolution of considerably more than 1000 cal/g-mole. These results lend support to the hypothesis that as-deposited chemically reduced Ni is an undercooled liquid.

Summary

The Ni deposit containing 7–10 w/o P produced by the catalytic Ni deposition process has been found to possess a dense, amorphous, liquid-like structure. It is probably the first occurrence of an amorphous metallic solid in massive form. The structure is unrelated to the nature of the substrate, manner of preparation, and thickness. The deposits were shown to conform, within microscopic resolution, exactly to the surface contour of the substrate. The deposit itself showed no porosity but in the etched state revealed striations in etching intensity and growth faults originating from asperities in the substrate surface. These striations in etching intensity were interpreted as banded variations in P content.

The as-deposited state of chemically reduced Ni is highly metastable and at 300°C or above reverts rapidly to the equilibrium condition of a phase mixture of crystalline Ni and crystalline Ni_3P. The dispersion of Ni_3P in Ni can be used as a means for promoting and controlling hardness of heat treated chemically reduced Ni.

Acknowledgments

This work represents part of a program sponsored by the General American Transportation Corporation at the Armour Research Foundation, and their permission to publish is gratefully acknowledged. Some of the x-ray diffraction studies were conducted by Miss Irene Corvin. Mr. E. Klimek was responsible for the metallography. Useful discussion was contributed by Dr. R. J. Spraul and Mr. W. J. Crehan of the sponsoring company.

Manuscript received March 14, 1956. This paper was prepared for delivery before the San Francisco Meeting, April 29-May 3, 1956.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1957 JOURNAL.

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16. B. E. Warren, *J. Appl. Phys.*, **8**, 645 (1937).

QUALIFICATION OF NICHOLAS J. GRANT

Date of Birth:	21 October 1915
Place of Birth:	South River, New Jersey
Home Address:	10 Leslie Road, Winchester, Massachusetts
Office Address:	Massachusetts Institute of Technology, Cambridge, Massachusetts
Education:	B. S. Metallurgy - Carnegie Tech., Pittsburgh, Pennsylvania 1934-38
	Sc. D. Metallurgy - Massachusetts Institute of Technology, Cambridge, Massachusetts 1940-1944
Current Position:	Director: MIT's Center for Materials Science and Engineering (1968 to present)
	Professor: Department of Metallurgy and Materials Science (1945 - to present)
Previous Additional Positions:	Metallurgist - Bethlehem Steel Co., 1938-1940
	President: New England Materials Lab., Inc. 1956-1966
	Chairman of the Board - Tang Industries 1960-1962
	Technical Advisor: Investment Castings Institute 1950-1960

PX 8

Consulting (all annual retainer basis)

Present:	Corning Glass Works: since 1947
	Avesta Stainless Steel Co. (Sweden) since 1947
	Engineered Precision Casting Co. since 1950
	Reynolds Metals Co. since 1960
	Stellite Division, Cabot Co. since 1968
	Abex (Div. Ill. Central) since 1969
	Kennecott Copper Co. since 1971
	Martin Marietta since 1973

Consulting
Previous

Ticonium (Dental)
Monsanto
Lukens Steel Company
Jones and Laughlin Streel Company
Boeing Aircraft Company (Scientific Advisor)
Loomis Sayles Company (investments)
Pittsburgh-Corning Corporation
Brush Beryllium Company
Nemlab (Div. Teledyne Company)
Noethrop Aircraft (Scientific Advisor)
Raytheon
SKC-Div. A.Johnson Company (powder metallurgy)
Sandia Corp. (Div. Western Electric)
Oak Ridge National Laboratory
Corhart Ceramics
Aberdeen Proving Grounds
Nuclear Metals Company
Cabot Corporation

Government Advisory Groups

Oak Ridge National Lab. Review Panel
Technical Advisory Board: Nuclear Powered Aircraft
Commerce Department: High Speed Ground Transportation Committee
NACA (National Adv. Comm. on Aeronautics)
Chairman 4 years, member 23 years
Materials Committee
NASA (National Aeronautical and Space Agency)
Research Advisory Committee
Office of Naval Research - Res. Advisory Comm.
USN: Bureau of Ships - Res. Advisory Comm.
U. S. Army Res. (AMMRC)
Titanium Advisory Board
National Materials Advisory Board (NMAB)
Numerous Boards - chaired 3 different Panels

Current Advisory Committees

AMMRC (Watertown Arsenal) - Sagamore Conf.
AMMRC (Watertown Arsenal) - Portsmouth Conf.
ASTM - Committee on Research and Technical Planning (Vice-Chairman)
NASA Research Advisory Committee

Patents

25 U. S. Patents - numerous foreign patents (Many relating to the field of powder metallurgy)

Publications

Over 270 publications in U. S. and foreign journals; numerous book chapters
Co-authors of "Behavior of Materials at Elevated Temperatures", MIT Press, 1965

Honorary Societies

American Academy of Arts and Sciences
Tau Beta Pi
Theta Tau
Sigma Xi
Alpha Chi Sigma

Professional Societies

American Society for Metals
American Institute for Mining and Metallurgical Engineers
American Society for Testing and Materials
Institute for Metals - London
Powder Metallurgy - London

Awards

Carnegie Tech. Merit Award for Excellence in Teaching and Research
Investment Casting Institutes Distinguished Service Award
Best Paper - AIME
Fellow: American Society for Metals
Powder Metallurgy Fundamentals Lecturer:1960
Keynote Lecturer: 3rd Nordic Conf. Denmark 1972
Keynote Lecturer: Canadian Powder Metallurgy Conference (AIME) 1965

E 879

PX-9

December 30, 1971

Mr. Stonback
Ernest F. Fullam, Inc.
P.O. Box 444
Schenectady, N.Y. 12301

Dear Mr. Stonback:

As per our telephone conversations, I am enclosing three coatings on 1020 steel substrate for electron microprobe analysis. The samples are marked as No. 1, No. 2 and No. 3. They are in "as sprayed" condition as you requested.

Please analyze sample No. 1 for Nickel, Aluminum, Nickel Aluminide, Nickel Oxide and Aluminum Oxide. Nickel Aluminide may be in the form of NiAl, $NiAl_3$ or Ni_3Al.

Samples No. 2 and No. 3 are very similar to No. 1 but we want to determine the amount of lead and chromium in the elemental state or in the oxide state.

Please advise cost prior to initiating work.

Very truly yours,

EUTECTIC CORPORATION

MP:hpc
enc.

Mahesh Patel

5044

E 880

PX-10

SCIENTIFIC CONSULTANTS

ERNEST F. FULLAM, INC.

ELECTRON MICROSCOPY · DIFFRACTION · MICROPROBE ANALYSIS

P.O. BOX 444 · SCHENECTADY, NEW YORK 12301 · 518/765-3933

January 18, 1972

Dr. Mahesh Patel
Eutectic Corporation
40-40 172nd Street
Flushing, New York 11358

References: Letter M. Patel to I. T. Stoneback of 12/30/71
Quotation #03507 of 1/5/72
Purchase Order No. 67098 of 1/10/72
EFF, Inc. Job #1476

Dear Dr. Patel:

The report concerning the three coated steel samples is attached to this letter. The analysis was done using X-ray diffraction, energy dispersive analysis, and electron microprobe analysis.

We trust the results will be helpful to you, and if we can be of further service to you, please do not hesitate to write or call.

Very truly yours,

ERNEST F. FULLAM, INC.

S. E. S. / lgd

Selby E. Summers

Louis M. Osika

Louis M. Osika

SES:lgd
Attachment

50430

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Scientific Consultants
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E 881

X-Ray Diffraction & Electron Microprobe Analysis of Coating on 1020 Steel Substrate

for

Eutectic Corporation
Flushing, New York

Report #1476 January 18, 1972

50431

ERNEST F. FULLAM
INCORPORATED
Scientific Consultants
P.O. BOX 444 • SCHENECTADY, N. Y. 12301

E 882

For: Eutectic Corporation
Flushing, New York
January 18, 1972

X-RAY DIFFRACTION AND ELECTRON MICROPROBE ANALYSIS OF COATING ON 1020 STEEL SUBSTRATE

Three samples of coated 1020 steel were submitted for both X-ray diffraction and electron microprobe analysis. These were designated as samples No. 1, No. 2, and No. 3 in letter from Dr. Patel dated December 30, 1971.

The purpose of the analysis was to examine sample No. 1 for compounds of nickel and aluminum such as NiAl, $NiAl_3$, or Ni_3Al, as well as other compounds of nickel and aluminum. The other two samples were to be analyzed for chromium and lead.

The sprayed coating on sample No. 1 was analyzed by X-ray diffraction and found to consist mainly of elemental nickel with a trace amount of γ-aluminum oxide. A standard diffractometer analysis detected only elemental nickel, but on examining the coating in a scanning electron microscope, particles of a non-conducting material were apparent. A typical area is shown in Figure 1. Energy dispersive X-ray analysis on these particles indicated they were very high in aluminum, whereas the matrix (positions 1, 2, and 7 on the micrograph) material showed relatively small amounts of aluminum. A Debye-Scherrer pattern was run of the scrapings taken from the surface of the sprayed coating. The resulting

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powder pattern registered three very weak lines besides the strong elemental nickel lines, and they were identified as γ-aluminum oxide. The data and the appropriate identification of the X-ray pattern is shown in Table I appended to this report.

Samples No. 2 and No. 3 were analyzed with the electron microprobe for chromium and lead. Both samples were polished in cross section in preparation for the analysis. A 30 micron diameter beam was used in order to obtain an average concentration since the chromium and lead were not homogeneous in the sample. An example of a chromium rich phase is shown in Figure 2. The micrographs show the topography of the polished surface and the variations in composition. The dark areas are either voids or elements with low atomic number. The 1020 steel is in the lower left corner. From the composition picture, we can see grey phases, which, in some cases, are rich in chromium judging from the X-ray image shown in Figure 2.

The lead and chromium concentrations shown in Table II were obtained by point counting 100 seconds at each point and relating the intensity to pure material. Sample No. 2 seemed to have greater segregation of chromium than sample No. 3. In one case, the chromium went as high as 16 percent.

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E 884

This particular spot is shown in the brightest area of the X-ray image shown in Figure 2. The lead concentration seemed to be more uniform, as shown in the included data.

Although the average value is shown in Table II for each sample and each element, it must be realized that the segregation shown would make it difficult to obtain a concentration representing the overall coating. This is particularly true for sample No. 2. However, the data does show there is more chromium and lead in sample No. 2 than in No. 3.

S. E. S. / bmb

Selby E. Summers

Louis M. Osika

Louis M. Osika

50435

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E 885

TABLE I

Customer Eutectic Corporation
Job No. 1476
Sample No. No. 1
Date 1/18/72

IDENTIFICATION

OBSERVED		Card No. 4-0850 Ni		Card No. 10-0425 γ-Al_2O_3		Card No.		Card No.	
d Å	I/Io	d Å	I/Io	d Å	I/Io	d Å	I/Io	d Å	I/Io
2.38	VVW			2.39	100				
2.03	VS	2.034	100						
1.98	VVW			1.977	100				
1.76	S	1.762	42						
1.39	VVW			1.395	100				
1.245	MS	1.246	21						
1.065	MS	1.0624	20						
1.018	W	1.0172	7						
0.880	W	0.8810	4						
0.810	WM	0.8084	14						
0.790	VW	0.7880	15						

50436

RADIATION CuKα EXPOSURE TIME 8 hrs. CAMERA DIA. 114.6

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TABLE II

Concentration in Weight Percent of Lead and Chromium in Coatings on 1020 Steel Substrate

	Sample No. 2		Sample No. 3	
	Cr	Pb	Cr	Pb
	0.2	0.4	0.2	0
	4.2	0.4	0.2	0.03
	0.1	0.4	0.4	0.13
	0.5	0.3	0.1	0.08
	0.6	0.3	0.1	0.13
	0.5		0.4	
	0.4		0.2	
Avg.	0.9	0.4	.2	0.07
	0.4*			

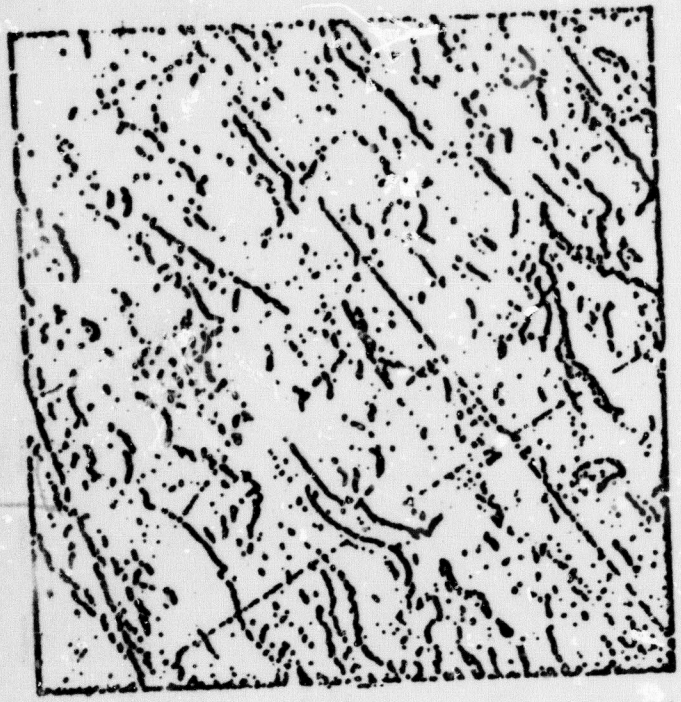
*Average omitting 4.2% from total

E 887

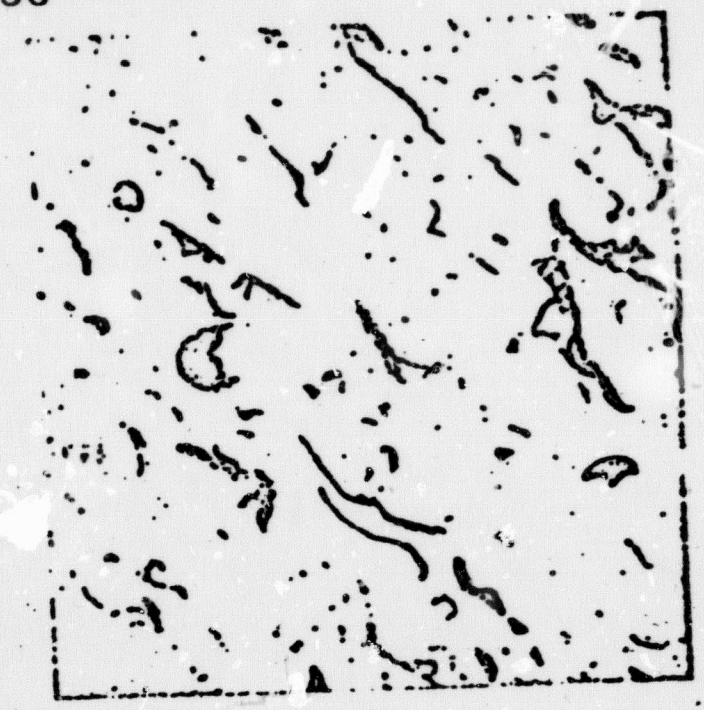
011172-1 300X

Figure 1 - SEM Micrograph of Sample No. 1

50438



011172-1 Topography 300X



011172-2 Composition 300X

011172-3 Chromium X-ray 300X

Figure 2 - Scanning Images of Sample No. 2 Showing Topography, Composition, and X-ray Image for Chromium

E 889

PX-11

May 30, 1967 F. J. DITTRICH ETAL 3,322,515

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Filed March 25, 1965

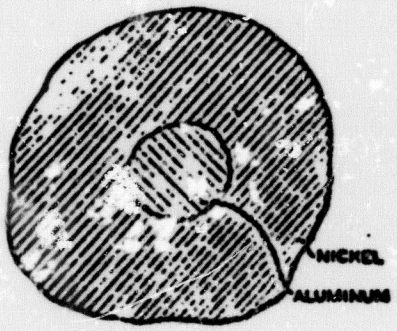


Fig. 1

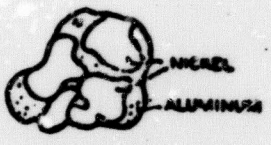


Fig. 2.

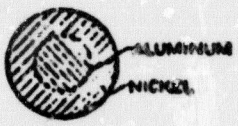


Fig. 3

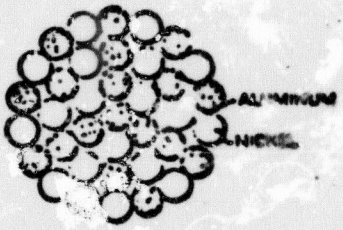


Fig. 4

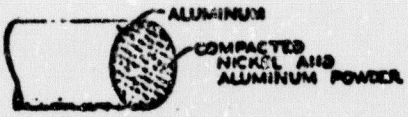


Fig. 5

INVENTORS

FERDINAND J. DITTRICH

ARTHUR R. SIMPARD

BY Burgess, Dinklage & Sprung

ATTORNEYS

E 890

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,322,515 May 30, 1967

Ferdinand J. Dittrich et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 49, strike out "the", second occurrence; column 7, line 5, for "as" read -- at --; line 7, for "deposite" read -- deposit --; line 69, for "aluminum" read -- alumina --; column 9, line 6, for "sprayer" read -- sprayed --; column 16, line 75, for "reactiing" read -- reacting --.

Signed and sealed this 5th day of December 1967.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents

E 891

United States Patent Office

3,322,515

Patented May 30, 1967

1

3,322,515

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Ferdinand J. Dittrich, Baltimore, and Arthur P. Shepard, Flushing, N.Y., assignors to Metco, Inc., a corporation of New Jersey

Filed Mar. 25, 1965, Ser. No. 442,727

28 Claims. (Cl. 29—191.2)

This is a continuation-in-part of copending applications, Ser. No. 72,543, filed Nov. 22, 1960, now abandoned; Ser. No. 134,544, filed Aug. 16, 1961, now Patent No. 3,254,970; Ser. No. 237,786, filed Oct. 26, 1962, now abandoned; and Ser. No. 343,705, filed Feb. 10, 1964.

This invention relates to the flame spraying of exothermically reacting intermetallic compound forming composites. The invention more particularly relates to the flame spraying of flame spray materials in the form of composites containing two or more components which will exothermically react with each other during the spraying, forming one or more intermetallic compounds, and to a novel group of such composites including powders and wires.

Flame spraying involves the feeding of a heat-fusible material into a heating zone, wherein the same is melted or at least heat-softened, and then propelled from the heating zone in a finely divided form, generally onto a surface to be coated.

The material being sprayed is generally fed into the heating zone in the form of either a powder or a wire (the latter term designating both rods and wires). The spraying is effected in a device known as a heat-fusible material spray gun or a flame spray gun.

In the wire type flame spray gun the rod or wire of the material to be sprayed is fed into the heating zone formed by a flame of some type, where it is melted or at least heat-softened and atomized, usually by blast gas, and thence propelled in finely divided form onto the surface to be coated. The rod or wire may be a conventionally formed rod or wire of a metal, or may be formed by sintering together finely divided material, or by bonding together finely divided material by means of a plastic binder or other suitable binder which disintegrates in the heat of the heating zone, thereby releasing the material to be sprayed in finely divided form.

For spraying finely divided, i.e., powdered material, a powder type flame spray gun is used in which the powder, usually entrained in a carrier gas, is fed into the heating zone of the gun formed by a flame of some type. The powder is either melted or at least the surface of the grains heat-softened in this zone, and the thus thermally conditioned particles propelled onto a surface to provide a coating. In the powder type spray gun as no "atomizing" energy is required, a separate blast gas is often dispensed with, though the same may be supplied in order to aid in accelerating the particles and propelling them toward the surface to be coated.

The blast gas may be provided for both the wire type and powder type guns to perform the additional function of cooling the workpiece and the coating being formed thereon.

The heat for the heating zone is most commonly produced from a flame caused by the combustion of a fuel, such as acetylene, propane, natural gas, or the like, using oxygen or air as the oxidizing agent. The heat may, however, also be produced by an electrical arc flame or, in the newer type of guns, by a plasma flame. The plasma flame may in itself constitute part of an electric arc, or, in accordance with a newer development, may be in the form of a "free plasma stream," i.e., a stream of plasma

2

which may be considered independent of the arc as it does not contribute to the electric flow between electrodes.

Heat-fusible material spray guns utilizing electric resistance heating or induction heating as the heat source have also been proposed but have not proven commercially successful except in connection with the spraying of low melting point metals, such as solders, lead or tin.

Flame spraying in the initial stages of its commercial development was used mostly for the spraying of various metals and was often referred to as metallizing. However, the art of flame spraying extends to the spraying of a much wider group of materials, including higher melting point or refractory metals, ceramics, cermets, and the like, and such materials are of increasing commercial interest.

In the case of spraying heat-fusible materials in the initial form of a rod or wire, the rod or wire is generally of a single composition, i.e., in the form of a specific metal, alloy, ceramic, or the like. While it is true that rods or wires formed from finely divided material bound together with a binder of plastic or the like, as mentioned above, were known, the binder generally did not take part in the spraying or contribute to the coating, and merely served the purpose of maintaining the rod or wire in shape until fed into the heating zone.

In the case of flame spray powders, while powders formed of several constituents were known, the same were generally in the form of a powder mixture of the individual constituents or, at best, a particle aggregate.

One object of this invention is the spraying of the heat-fusible material in a novel form which allows the obtaining of superior results.

A further object of this invention is a novel group of flame spray materials.

These and still further objects will become apparent from the following description read in conjunction with the drawing in which:

FIG. 1 diagrammatically shows a cross-section of a grain of novel powder in accordance with the invention;

FIG. 2 is a cross-section of a further embodiment of an aggregate grain of novel flame spray powder in accordance with the invention;

FIG. 3 is a diagrammatic cross-section of an embodiment of a novel flame spray wire in accordance with the invention;

FIG. 4 shows a cross-section of a further embodiment of a novel flame spray wire in accordance with the invention; and

FIG. 5 shows a still further embodiment of a novel flame spray wire in accordance with the invention.

In accordance with the invention, the flame spraying is effected with the heat-fusible material in the form of a composite containing at least two components which will exothermically react with each other at the temperatures developed during the spraying, forming an intermetallic compound.

The term "composite" as used herein is intended to designate a structurally integral unit and does not include a mere mixture of components which may be physically separated without any destruction of the structure. Thus, in the case of powder, the term "composite" does not include a simple mixture of individual granules of the separate components, but requires that each of the individual granules contain the separate components which will exothermically react, forming intermetallic compounds. In the case of wire, the individual components must be incorporated in a single wire. In the composite the components must be in intimate contact with each other.

In connection with powders, each grain may consist of an aggregate containing the two components which

will exothermically react, forming the intermetallic compound, but preferably the individual grains of the powder are in the form of a clad composite consisting of a nucleus of one of the components and at least one coating layer of the other component. Alternatively, the composite may consist of separate, concentric coating layers of the two components and a nucleus of still a third material.

In the case of wires, the composites may be in the form of a wire having a coating sheath of one material and a core of the other, alternate coating sheaths of the components and a core of a third material, a wire formed by twisting or rolling separate wire strands of the components, a wire consisting of a sheath of one component and a core containing the other component in powder or compacted form, a wire consisting of a sheath of one component and a core containing a compacted powder mixture of this same component material and one or more other components, a wire consisting of a plastic sheath and a core containing a compacted powder mixture of components, etc.

In order for the wires to be satisfactory for spraying, the same must not cavitate at the tip when heated, and should preferably be capable of forming a pointed or slightly tapered tip when being melted and sprayed. Thus, if the wires have an outer layer or sheath of one component and an inner core of another component, the inner core cannot have a lower melting point than the outer sheath, as otherwise the inner core will initially melt, causing cavitation at the tip. For example, if the wire is composed of nickel and aluminum as the exothermically reacting components and is in the form of a core with a coating sheath, the core must be nickel and the coating sheath aluminum, as otherwise during the spraying the core will initially melt out, causing the cavitation which will interfere with a satisfactory spraying operation. The wire having the melting-point characteristics so as to allow the melting off of the tip without this cavitation, is referred to herein and in the claims as "non-cavitating wire."

As the components, any two metallics which may be melted together to form an intermetallic compound in an exothermic reaction may be used. The components should release about 3000 calories per gram atom, and preferably at least 7500 calories per gram atom in the exothermic reaction forming the intermetallic compounds. The term "calories per gram atom" as used herein denotes the number of gram calories which the average atomic weight in the grams of the intermetallic compound formed will generate in so being formed. While the components are preferably present in the stoichiometric proportions required for the formation of the intermetallic compound, it is, however, possible to also have an excess of one or the other provided the relative amounts are sufficient to release the quantities of heat indicated above in the formation of the intermetallic compounds.

An extremely large number of metal components are known which can be melted together in an exothermic reaction, forming an intermetallic compound with the generation of heat. Any of these component pairs may be utilized in accordance with the invention, it only being required that the same be capable of being initially formed into the composite suitable for spraying and that the intermetallic compounds formed therefrom liberate the required amount of heat in the intermetallic compounds-formation and are suitable as components of a sprayed coating. As a general rule, components which will form intermetallic compounds having a higher melting point will liberate sufficient heat to be useful in accordance with the invention. In certain instances, however, components which will form intermetallic compounds which do not have as high a melting point, will also liberate sufficient heat in the exothermic reaction and thus be useful. Preferred components are aluminum with at least one of Co, Cr, Mo, W, Ta, Nb, Ti, or most preferably Ni; or silicon with at least one of Ti, Nb, Cr, W, Co, Mo, Ni or Ta.

While iron itself is not a satisfactory component, the same may be present in addition to another component, which in itself is satisfactory, such as in the form of an alloy therewith. This other component, however, must be present in amount sufficient to form the intermetallic compound with the other component of the composite, with the generation of sufficient heat to aid the spraying operation. Thus, for example, iron which just contains enough alloyed nickel to render the same rust-resistant, does not contain enough nickel for an effective exothermic reaction with aluminum. Generally an alloy if nickel and iron must contain at least about 12% nickel for this purpose.

FIG. 1 shows a composite powder consisting of a nucleus of aluminum and a coating layer of nickel. FIG. 2 shows an aggregate of these components; and FIGS. 3, 4, and 5 show various forms of wire containing these components, FIG. 3 showing a wire having an aluminum core with a nickel sheath. FIG. 4 showing a wire made of alternate strands of nickel and aluminum wire, as for example 18 strands of 25 gauge (.012" diameter) nickel wire, and 19 strands of 25 gauge aluminum wire; and FIG. 5 shows a sheath of aluminum filled with granules of nickel and aluminum.

Where one of the component metals is available as a metal hydride, the same may be used in this form rather than as a metal per se. When flame sprayed the hydrogen gas evolved from the hydride produces a reducing atmosphere, which in turn suppresses oxidation of the intermetallic compounds during and immediately after their formation. Thus, for example, in place of titanium, titanium hydride may be used as one of the components.

Also for the purpose of reducing oxidation a metal hydride, such as titanium hydride, may be added in a minor amount to the other components. Thus, for example, 1–10% by weight, and preferably 1–5% by weight, based on the total of the hydride and other components, may be used.

In addition, the powder granules and the wire may contain other conventional flame spray components, or be sprayed in admixture or in conjunction therewith. Thus, for example, the coated powders may additionally contain other coating layers of other flame spray components or may contain a nucleus of another flame spray material with alternate coating layers of the components which will exothermically react, forming the intermetallic. In a similar manner, the aggregates or the wires may contain further flame spray components, and in the case of powders, the same may additionally be admixed with any other desired flame spray powder.

The clad powders, in accordance with the invention, may be formed in any known or desired manner, and preferably by the known chemical plating processes in which coating material is deposited on a seed or nucleus of another material, or in which multiple layers of various materials are built up on the seed material, or in which various materials are co-deposited in a single layer on the seed material.

A mode of forming the clad powders involves the depositing of a metal from a solution by reduction on a seed or nucleus, such as by the hydrogen reduction of ammoniacal solutions of nickel and ammonium sulfate on a seed powder catalyzed by the addition of anthraquinone. It is also possible to form the coating by the use of other known coating processes, such as coating by vapor deposition, by the thermal decomposition of metal carbonyls, by hydrogen reduction of metal halide vapors, by thermal deposition of halides, hydrides, carbonyls, organometals, or other volatile compounds, or by displacement gas plating and the like.

A preferred and greatly simplified mode of forming the clad powders in accordance with the invention is the depositing of one component as a coating in the form of a paint on the other component. Thus, one of the components which is to form the coating or cladding, may be dispersed in finely divided form in a binder or lacquer so as, in effect, to form a paint in which this component corresponds to the pigment. The paint is then used to coat core particles of the other component and the binder or lacquer allowed to set or dry. The binder material is preferably a resin which does not depend on solvent evaporation in order to form a dried or set film, and which film will decompose or break down in the heat of the spraying process. The binder, for example, may be a phenolic varnish or any other known or conventional varnish, preferably containing a resin as the varnish solids. The component which is initially mixed with the binder or varnish should preferably be as finely divided as possible, as for example —325 mesh. The other component which constitutes the core should be approximately or only slightly below the particle size ultimately desired for the spray powder. The coating of the core component with the "paint" may be effected in any known or desired manner, and it is simply necessary to mix the two materials together and allow the binder to dry or set, which will result in a fairly free-flowing powder consisting of the core component coated with a cladding of the other component bound in the powder.

The aggregates may be formed by compacting or briquetting the various components into the individual granules, or into larger aggregates and then breaking these aggregates into the granules.

The wires may be formed in the known conventional manner for forming wires with various components as, for example, by shrinking a sheath on a core, by forming the core with powder, by twisting the component wires, followed by rolling, drawing, swaging, or the like if desired.

In accordance with one mode of manufacture, one of the components may be formed into a tube or sheath and filled with a powder of the other component or a powder comprising a mixture of the two components, or containing additional components. The tube ends are then sealed and the wire reduced to the desired wire diameter by swaging, rolling or drawing. Preferably the powder or powder mixture is first compressed into cylindrical briquettes before being placed in the sheath or core. The sealing of the tube ends after loading with the powder or powder mixture can be effected, for instance, by insertion of a plug, for example of the metal of the sheath, by welding, twisting, crimping, or the like.

Powders in accordance with the invention should have the general over-all shape and size of conventional, flame-spray powders, and thus for example should have a size between —60 mesh and +3 microns and preferably —140 mesh and +10 microns (U.S. Standard screen mesh size). Most preferably the powder should be as uniform as possible in grain size, with the individual grains not varying by more than 250 microns and preferably 75 microns.

Depending on the particular flame spray process and the desired purpose, the composite powders may be sprayed per se or in combination with other different composite powders, or in combination with other conventional flame spray powders or powder components.

While the powders are preferably sprayed, as such, in a powder-type of flame spray gun, it is also possible to combine the same in the form of a wire or rod, using a plastic or similar binder, which decomposes in the heating zone of the gun, or in certain cases the powders may be compacted and/or sintered together in the form of a rod or wire. The wires must have the conventional sizes and accuracy tolerances for flame spray wires, and thus for example may vary in size between ¼" and 20 gauge, and are preferably of the following sizes: ⅛" +.0005" to —.0025", ⅛" +.0005" to —.0025", 11 gauge +.0004" to —.0025", and 15 gauge +.001", with a smooth, clean finish free from surface marks, blemishes, or defects. The wires are sprayed in the conventional manner, using conventional wire-type flame spray guns.

In combining, in the exothermic reaction, forming the intermetallic compound, the components generate heat in situ in the actual material which is to form at least a part of the coating. This is to be distinguished from flame-spray processes and materials in which heat is generated by a reaction, such as an oxidation reaction, in which a foreign and non-metallic element is introduced and in which undesirable components may be produced. Aside from greatly contributing to the thermal efficiency of the process, the heat generated in situ in the formation of the intermetallic compound produces novel results, in many instances forming a denser, more adhering coating, having characteristics of at least a partially fused coating. In many instances the coating has self-bonding characteristics, so that special surface preparation, other than a good cleaning, is not required. The spraying in all other respects is effected in the conventional, well-known manner, using conventional flame spray equipment, and the conventional surface preparation may be utilized, if desired. The composites in accordance with the invention may be sprayed in conjunction with, or in addition to, other flame spray materials conventionally used in the art, or may be sprayed in combination or conjunction with the others.

The use of the composites as, for example, the nickel-aluminum composites, will generally improve the bond of the total sprayed material, and thus of the other component or components to the substrate, sometimes making the mixture self-bonding. The particle bond will be improved and the coating will be denser, so that its porosity may be decreased. In general, as little as 10% by weight of the composites in accordance with the invention will be sufficient to substantially improve the bonding characteristics and decrease the porosity of other flame-spray materials, such as conventional flame spray metals, alloys or ceramics. There is, of course, no upper limit on the amount, as the composite may be sprayed per se, but generally at least about 20% by weight of the other component is required if this component is to have a pronounced effect on the characteristics of the coating.

The following examples are given by way of illustration and not limitation:

Example I

(a) An aluminum powder having a particle size between —140 mesh and +325 mesh (U.S. Standard screen size) is coated with nickel in the known manner by the hydrogen reduction of an ammoniacal solution of nickel and ammonium sulphate using anthraquinone as the coating catalyst. The reduction is effected at a temperature between about 200 and 350° F. in a mechanically agitated autoclave using solutions containing 45–80 grams per liter of nickel and 10–400 grams per liter of $(NH_4)_2SO_4$ and 20–30 grams per liter of NH_3. About .2 gram per liter of anthraquinone is used as the catalyst and the autoclave is pressurized with hydrogen at a pressure of about 300 lbs. p.s.i.g. After the nickel solution is depleted and the aluminum coated with an initial coating of nickel, the solution is discharged from the autoclave and replenished with a fresh solution which need not contain further amounts of the anthraquinone coating catalyst, as the initially formed nickel coating in itself acts as a catalyst. The cycle is continuously repeated until a composite powder is formed containing about 16 to 18% by weight aluminum and 84 to 82% by weight of nickel, and a size of —100 to +270 mesh.

The powder thus formed is flame-sprayed on a mild steel plate which has been surface-cleaned with emery cloth. The spraying is effected at about 9 inches from the plate, using a powder-type flame-spray gun as described

in U.S. Patent 2,961,318, issued Nov. 22, 1960, and sold by Metco Inc. of Westbury, Long Island, under the trade name of "Thermospray" powder gun. The spraying is effected at a rate of 6 to 9 lbs. of powder per hour, using acetylene gas as the fuel at a pressure of 10 p.s.i. and a flow rate of 17 to 25 cu. ft./hr. and oxygen as the oxidizing gas at a pressure of 12 p.s.i. and a flow rate of 29 to 35 cu. ft./hr.

The nickel coating and the aluminum base combine in the heat of the flame with a strong exothermic action, forming a mixture of nickel aluminum intermetallic compounds which deposits on the base as a dense, high quality coating which exhibits self-bonding characteristics. A coating layer of .002"–.004" thickness is built up in this manner. The coating may be used as a base material for spraying of further layers of different metals or the like, and serves as an excellent intermediate bonding layer.

The coating layer may also be built up to a greater thickness as, for example, .010"–.020", for use as an oxygen barrier undercoat, or to even greater thickness as, for example, .020"–.030" or thicker as a wear-resistant-oxidation-resistant surface.

Due to its self-bonding characteristics the sprayed coating will adhere to a base without the conventional surface preparation or roughening, and due to the natural characteristics of a sprayed material, will allow further materials to be sprayed thereon with good bonding. The coating formed from the powder has excellent oxidation-resistant characteristics even at high temperatures and in oxidizing atmospheres, and will for example prevent the oxidation of base materials, such as molybdenum or the like. The sprayed coatings may be used as a lining in metal-melting crucibles or molten metal-handling equipment, and will not be wetted or penetrated by many molten metals, including self-fluxing alloys. Coatings formed of the sprayed material also show good potential as high temperature, wear-resistant coatings.

When the example is repeated on a molybdenum rod of ¼" diameter, with a coating between .010"–.012" thick, the coated rod may be repeatedly heated to approximately 2000° F. in air, in an electric furnace and cooled to room temperature with no visible oxidation occurring.

Similar results may also be obtained if the composite powder contains 10–45% by weight of aluminum and 55–90% by weight of nickel.

(b) Example 1(a) is repeated, using, however, cobalt in place of the nickel. Comparable results are obtained.

(c) Example 1(a) is repeated, using titanium hydride (TiH_2) powder in place of the aluminum and in an amount of 25–85 weight percent, and preferably 60–85 weight percent of the total. The coating formed upon spraying is hard and dense, and when sprayed on a smooth, pressed and sintered Al_2O_3 substrate, an excellent bond is formed. The spraying may be effected with an oxygen-hydrogen or oxygen-acetylene flame.

Example 2

Example 1 is repeated with the spraying being effected in turn on the following bases and prepared in the following manner:

Low alloy steels and stainless steels, smooth-ground to remove surface contamination; copper and copper base alloys, rough-ground or light-grit-blasted; aluminum and aluminum base alloys, rough-ground or light-grit-blasted; magnesium, rough-ground or light-grit-blasted; and titanium, rough-ground or light-grit-blasted.

In each case when a further material, such as aluminum or the like, was sprayed over the coating in the conventional and well known manner, the same bonded with a tenacious bond, though if this material had been initially sprayed on the surface as prepared in the manner indicated above, a satisfactory bond would not be obtained.

Example 3

The nickel-clad powder of Example 1 is mixed with an Al_2O_3 powder having a particle size between 62 microns and 10 microns, in the ratio of about 40% of the nickel-clad powder with 60% by weight of the ceramic. The powder is sprayed, using the gun described in Example 1, on a mild steel plate which has been surface cleaned by smooth grinding. Spraying is effected at a distance of about 9" from the plate at a rate of about 4 to 8 lbs. of powder per hr., using acetylene at a pressure of 10 lbs. p.s.i. and a flow rate of 17–25 cu. ft./hr., and oxygen at a pressure of 12 p.s.i. and a flow rate of 29–35 cu. ft./hr.

A self bonding cermet coating is formed which showed excellent thermal shock-resistance, hardness, erosion-resistance, and which strongly inhibited oxidation of the base.

It is possible to vary the percentages of the ceramic in the mixture between 5 and 85% in order to vary the properties of the coating. With an increased amount of the intermetallic compound in the cermet coating formed, the bonding and thermal shock-resistant properties increased, whereas with an increased amount of the ceramic, the hardness and wear-resistant properties of the coating are increased and the thermal conductivity decreased.

Example 4

Example 3 is repeated, using the following materials in place of the aluminum oxide:

Zirconia, calcium zirconate, magnesium zirconate, spinel, ceric oxide, hafnium oxide, rare earth oxides, molybdenum disilicide, tungsten silicide, chromium oxide, titanium silicide, tungsten carbide, titanium carbide and chromium carbide.

In each case an excellent coating was formed.

Example 5

A nucleus of silicon powder is coated with nickel to form a nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 75–85% nickel based on the silicon-nickel total. The composite powder is sprayed with the flame spray gun described in Example 1 on a steel base prepared by lightly grit-blasting, using the spraying conditions as described in Example 1. During the spraying silicon combines with the nickel in an exothermic reaction, greatly enhancing the thermal efficiency of the spraying and producing an excellent coating.

Example 6

Titanium is coated with nickel as described in Example 1 to produce a powder having a particle size between 100 and 325 mesh and containing 10 to 80% nickel based on the titanium-nickel total.

The nickel protects the titanium from oxidation during storage and when spraying.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the nickel and titanium combine exothermically in the flame to form a corrosion-resistant coating comprising a nickel-titanium intermetallic compound.

Example 7

Tellurium powder was coated with copper so as to form a composite having a particle size between 100 and 325 mesh and containing 30 to 80% copper based on the tellurium-copper total.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the copper and tellurium combine to form a new material.

During the spraying heat was evolved upon the combination of the copper and tellurium increasing the thermal economy of the process.

Example 8

The nickel clad flame spray power of Example 1 is mixed with about 20% by weight of low pressure polyethylene powder and molded at a temperature of about 212° F. into the form of a rod of ⅛" diameter. The rod is sprayed, using a conventional wire-type flame spray gun sold by Metco Inc. of Westbury, N.Y., as the Metco type 4-E gun. The spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu. ft./hr. with oxygen as oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu. ft./hr.; with air as a blast gas at a pressure of 30 p.s.i. and a flow rate of 25 cu. ft./min. The end coating produced is similar to the coating produced in Example 1.

Example 9

A wire is formed by encasing a core of nickel in a tube of aluminum and drawing to a size of .125" in diameter plus or minus .002". The wire contains 82 to 84% by weight of nickel based on the aluminum-nickel total.

The wire is sprayed, using a conventional wire type flame spray gun sold by Metco Inc. of Westbury, N.Y., as the Metco type 4-E gun. Spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu. ft./hr. with oxygen as the oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu. ft./hr. Air is used as a blast gas at a pressure of 55 p.s.i. and a flow rate of 30 cu. ft./min. The end coating produced is similar to the coating produced in Example 1.

Similar results are also obtained using 55-90% by weight of nickel in the wire.

Example 10

A composite wire is formed by winding individual wires of nickel and aluminum to form a stranded wire with a diameter of .125" plus or minus .002". The wire contains 55 to 90% by weight of nickel based on the total Al-Ni. The wire is sprayed in the manner described in Example 9, with identical conditions and coating resulting.

Example 11

A silicon powder having a particle size between 140 and 325 mesh is coated with molybdenum in the known manner and a composite powder is formed containing about 38 to 39% by weight of silicon and about 61 to 62% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The molybdenum coating and the silicon base combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

Example 12

A molybdenum powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, N.Y., under the trade name of type 2MB Plasma Flame gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using a mixture of argon and hydrogen gas as the plasma gas, with argon at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., and hydrogen at 50 p.s.i. and a flow rate of 25 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu. ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 460-500 amperes at 57-62 volts.

The molybdenum base and silicon coating combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

Example 13

A silicon powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The chromium coating and the silicon base combine in the heat of the flame, forming a chromium-silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

Example 14

A chromium powder having a particle size between 140 and 325 mesh is coated with silicon in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of type 2MB Plasma Flame gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu. ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 460-500 amperes at 57-62 volts.

The chromium base and silicon coating combine in the heat of the flame, forming a chromium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

Example 15

A zirconium powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner and a composite powder is formed containing about 40% zirconium and 60% chromium by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material in the manner described in Example 1.

The chromium coating and the zirconium base combine in the heat of the flame, forming a chromium zirconium intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures.

Example 16

A titanium powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 65% titanium and 35 to 65% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting.

The spraying is effected at about five inches from the plate, using a powder type plasma flame spray gun sold by Metco Inc. of Westbury, N.Y., under the trade name of type 2MB Plasma Flame gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft. hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu. ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57-62 volts.

The titanium base and silicon coating combine exothermically in the heat of the flame, forming a titanium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

Example 17

A dysprosium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 60 to 75% dysprosium and 25 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The aluminum coating and the dysprosium base combine in the heat of the flame with a strong exothermic action, forming a dysprosium aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

Example 18

A lanthanum powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 70 to 75% lanthanum and 25 to 30% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the lanthanum base combine exothermically in the heat of the flame with a strong exothermic action, forming a lanthanum aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

Example 19

A chromium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed consisting of 60 to 62% chromium and 38 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the chromium base combine in the heat of the flame with a strong exothermic action, forming a chromium aluminum intermetallic compound which deposits on the base as a dense, high quality coating of very high melting point and excellent oxidation-resistance.

Example 20

Example 19 is repeated except that the composite powder is formed with an aluminum core and chromium coating. Identical results are obtained.

Example 21

The nickel-clad aluminum composite powder of Example 1 is mixed with cobalt bonded tungsten carbide particle powder having a particle size range of −140 mesh +10 microns, and preferably −140 +325 mesh in proportions of:

(a) 80 weight percent tungsten carbide to 20 weight percent of the composite.

(b) 20 weight percent of the carbide to 80 weight percent of the composite, and

(c) preferably 50 weight percent each of the tungsten carbide and composite.

The powder mixtures are each flame-sprayed on a mild steel plate which has been surface-cleaned by grinding or very light sand-blast cleaning. The spraying is effected at about 8-9 inches from the plate, using a gas-oxygen type flame-spray gun as described in U.S. Patent 2,961,335, issued Nov. 22, 1960, and sold by Metco Inc. of Westbury, N.Y., under the trade name of "Thermo-Spray" powder gun. The spraying is effected at a rate of 6 to 10 lbs. per hour using acetylene gas as the fuel at a pressure of 12 p.s.i. and a flow rate of 20 to 30 cu. ft./hr. and oxygen as the oxidizing gas at a pressure of 14 p.s.i. and a flow rate of 30 to 40 cu. ft./hr.

The nickel-aluminum composite powder in the mixture reacts exothermically in the flame to provide the self-bonding properties of the mixture and, being fully molten on impact with the substrate, becomes the matrix which securely binds the tungsten carbide particles together in the coating.

Used as sprayed, or finished by proper grinding procedure, the resultant coating is of a highly wear-resistant coating material, applicable to virtually any base material and not subject to the limitations of the previously used self-fluxing alloy matrix materials which must be fused at approximately 1900° F.

Example 22

Example 21 is repeated, except that in place of the grade of tungsten carbide cobalt powder grains used, cobalt-bonded tungsten carbide grains with lower cobalt content and sharp, angular shape are used.

The powder was sprayed in the manner described in Example 21. The sharp, angular edges of the initial tungsten carbide particles were retained in the coating.

The deposited coating may be suitably finished by grinding for use as a wear-resistant coating or used as deposited where the coated article is to be used as a knife or lip, the sharp edges of the carbide inclusions constituting the abrading or cutting edges.

Example 23

Example 22 is repeated except that in place of the tungsten carbide grains described, cobalt-bonded tungsten carbide particles of sharp, angular shape were used which were first coated with nickel in the manner described in Example 1, so as to produce nickel-clad particles having a size between 100 and 325 mesh and containing from 20-50% nickel based on the tungsten carbide-nickel total.

Example 24

The nickel-clad aluminum composite described in Example 1 is mixed with a columbium (niobium) powder of size between −120 mesh and +10 microns and preferably −140 +325 mesh in the proportions of 60 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and when properly finished, by grinding or other means, is a highly wear-resistant, hard coating.

Example 25

The nickel-clad aluminum composite described in Example 1 is mixed with a molybdenum powder of a size between −120 mesh and +10 microns and preferably −140 +325 mesh in the proportions of 65 weight percent molybdenum to 35 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self bonding to

a wide variety of substrate materials and when properly finished, by grinding or other means, presents a highly wear-resistant, hard surface.

Example 26

Example 21 is repeated except in place of the tungsten carbide, other carbides such as titanium carbide, tantalum carbide, columbium carbide, chromium carbide and mixtures of the various carbides are used.

Example 27

The nickel-clad aluminum core composite from Example 21 is mixed with aluminum powder in the mesh size range −100 +325 mesh, and preferably in the −170 +325 mesh size range in the proportions of 80 weight percent nickel aluminum composite to 20 weight percent aluminum.

The mixture was sprayed in the manner described in Example 21. The coating as deposited consists of an intimate mixture of the flame-reacted nickel aluminide and aluminum securely bonded to the base and particle to particle within the coating.

Upon heat-treating in the temperature range 1250° F. to 1500° F. in reducing atmosphere, dry hydrogen for instance, the nickel aluminide and aluminum combine to form a dense, homogenous coating fused to the base material which can be used for "cathodic" protection of iron and steel subject to water and salt-water corrosion.

Example 28

The nickel-clad aluminum composite powder of Example 21 is mixed with Monel powder of a size between −100 mesh and +10 microns, and preferably between −140 and +325 mesh in the proportions 35 weight percent composite to 65 weight percent Monel.

The powder mixture was sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and the inclusion of the nickel-aluminum composite, the components of which combine exothermically in the flame to provide the self-bonding ability of the mixture, considerably increase the particle to particle bonds within the coating and decrease the permeability of the coating.

Example 29

Example 28 is repeated except that nickel and stainless steel powders are substituted for the Monel.

Example 30

Example 28 is repeated except that chromium is substituted for the Monel.

The resultant coating when properly finished, by grinding or other means, shows high resistance to abrasion, wear, and galling by other metals, and is an excellent bearing surface.

Example 31

Finely divided aluminum powder (−325 mesh) was blended with a phenolic varnish having approximately 50% solid contents so as to form a mixture having the consistency of a heavy syrup and containing 60% by weight of the metallic aluminum.

100 grams of this varnish aluminum powder mixture was added to 240 grams of nickel powder having a size between −200 and +325 mesh, and the two were thoroughly mixed, with the mixing continued until the varnish dried, leaving a fairly free-flowing powder in which all of the nickel core particles were clad with a dry film which consisted of aluminum particles bonded to each other and to the core material by the phenolic binder. The powder is then warmed to 250° F. to insure complete drying. There were some minor agglomerates which were screened out and handmilled to reduce the same to a −100 mesh powder. The end powder consisted of approximately 15 weight percent aluminum and 85 weight percent nickel due to the loss of some aluminum during the milling. The powder is sprayed in the manner described in Example 1 producing a similar coating bond, however, more than twice the tensile strength of the coating produced in Example 1.

Example 32

(a) A mixture of 6 weight percent aluminum and 94 weight percent nickel powder are thoroughly blended and pressed together in the form of cylindrical briquettes which are loaded into an aluminum tube of .375" inside diameter, after which the tube ends are welded closed. The 3/8" diameter feed stock is then swaged to 1/4" diameter, then to a 5/32" diameter then to a 1/8" finished wire diameter. The wire is then annealed and coiled. The wire is then sprayed, using the conventional wire type flame spray gun sold by Metco Inc. as the Metco type 4-E gun. Spraying is effected, using acetylene at a pressure of about 15 lbs. p.s.i. and a flow rate of 37 cu. ft./hr. and oxygen as the oxidizing gas at a pressure of 36 lbs. p.s.i. and flow rate of 75 cu. ft./hr. Air is used as a blast gas at a pressure of 55 lbs. p.s.i. and flow rate of 20 cu.ft./min. The wire is sprayed at a rate of 5 ft. per minute. The spray material is deposited on a surface of ground and machine-finished, cold rolled steel with a tensile bond strength of 3820 lbs. p.s.i. The sprayed coating is hard and dense; it is wear- and oxidation-resistant and it also could serve as a base for further spraying.

(b) Example 32(a) is repeated except that chromium is used in place of the nickel powder in amounts of from 24–95 weight percent, based on the total of the aluminum and chromium. Spraying results in a high quality coating which has self-bonding properties and is resistant to oxidation at high temperatures.

(c) Example 32(a) is repeated, using columbium powder in place of the nickel powder in amounts of from 40–90 and preferably 50–85 weight percent, based on the total of the columbium and aluminum. The sprayed coating formed is a high quality coating which is resistant to oxidation at high temperatures and may be used to protect tantalum and molybdenum bases from oxidation.

(d) Example 32(a) is repeated, using tantalum powder in place of the nickel powder in amounts of 40–90 weight percent and preferably 68–75 weight percent of tantalum, based on the total of tantalum and aluminum. The sprayed coating is a dense, high quality coating which is self-bonding and is resistant to oxidation at high temperatures.

(e) Example 32(a) is repeated, using boron powder in place of the nickel powder in amounts of 40–60 weight percent, based on the total of boron and aluminum. The resulting sprayed coating is self-bonding and is resistant to oxidation at high temperatures.

(f) Example 32(e) is repeated except that the powder additionally contains 0.5 to 5 weight percent of boron, and/or 0.5 to 5 weight percent of silicon, based on the total of the components. The coating formed is similar to that obtained in Example 32(e) except that on heating to high temperature in air, a very thin, dense, adherent, protective oxide film forms on the surface of the intermetallic compound formed, which is resistant to spalling due to thermal-shock, and which is believed self-healing.

(g) Example 32(a) is repeated except that tungsten carbide containing 12% binder and having a particle size below −140 mesh is added in amount of 5–70 weight percent, based on the total of the components. The resulting coating is a dense, extremely wear-resistant coating, which has self-bonding properties. This example may be further repeated, using in place of the tungsten carbide specified, crystalline tungsten carbide, aluminum oxide, diamonds or any other abrasive material.

(h) Example 32(a) is repeated. However, 1–10% by weight and preferably 1–5% by weight of titanium hydride of a size below −100 mesh and preferably below −325 mesh, based on the total of the components, is added to the core material. The results are the same as indicated

in Example 32(a) except that the coating formed is of improved physical strength, containing considerably less oxide inclusions. In place of the titanium hydride other metal hydrides may be used.

(i) Example 32(a) is repeated except that the nickel powder is replaced with a nichrome powder consisting of a chrome alloy containing 80% nickel and 20% chromium. When sprayed the wire gives a dense, self-bonding coating which is extremely oxidation-resistant.

(j) Example 32(a) is repeated except that the nickel powder is replaced with a powder mixture consisting of 80% by weight nickel and 20% by weight chrome. When sprayed the wire gives a dense, self-bonding coating which is highly oxidation-resistant.

Example 33

Table I below gives examples of further component pairs which may be used to form the powders and/or wires in accordance with the invention.

Each of the component pairs as listed in Table I below may be formed into a composite powder or wire as described above, and when flame-sprayed will exothermically react, forming an intermetallic compound and high grade coating. Thus, the component pairs may be formed into clad powders as described in Example 31 and sprayed as described therein, or formed into a composite wire as described in Example 32 and sprayed as described therein.

TABLE I

Al Cr	Al Cd	Be U	Ga Dy	Mg Sb	Si V
Al As	Al Ga	Be Zr	Ga Sb	Mg Sn	Si Zr
Al Au	Al In	Bi Cr	Ga Te	Na Pb	Sn Te
Al B	Al Mg	Bi Ce	Ga U	Na Sb	Sn U
Al Be	Al Zn	Bi K	Ge Mg	Na Se	Sn Zr
Al Ca	B Y	Bi Li	Ge Nb	Na Sn	Te Zn
Al Ce	B Ca	Bi Mg	Ge Zr	Nb Te	Mo Re
Al Co	B Na	Bi Na	Li In	Nb Ti	Nb Re
Al Cr	B Cr	Bi Sc	In Te	Nb Si	Ta Re
Al Fe	B Hf	Bi Sr	In Tl	Ni Th	V Re
Al Ir	B Nb	Bi Te	In Ru	Ni Y	Ti Re
Al La	B Ta	Bi Th	K Sb	Pb Ir	Ti Be
Al Mn	B Th	Ca Pb	K Se	Pb Pu	Cr Si
Al Mo	B Ti	Ca Sn	K Sn	Pb Zr	Cr Ti
Al Nb	B Tl	Ca Sr	K Tl	Pb Tl	Cr Zr
Al Ni	B V	Ca Tl	K U	Pd U	Mg Te
Al Pt	B W	Cd Li	La Pb	Pr Sn	Si Te
Al Ti	B Zr	Cd Na	La Sb	Pr Tl	Si Th
Al Zr	Ba Pb	Ce In	La Sn	Pr Tl	Si W
Al Sb	Ba Sn	Ce Mg	La Tl	Sb Zr	Si W
Al Cu	Be Sr	Ce Pb	La Zn	Se Sn	Co Si
Al Ca	Be Co	Ce Si	La Pb	Se Th	Mo Si
Al Te	Be Cr	Ce Sn	La Sb	Se Tl	Ni Si
Al U	Be Ni	Ce Tl	La Sn	Ga Te	Si Ta
Al V	Be Nb	Cr Zn	Li Tl	Si Ti	
Al W	Be Fe	Ga Na	La Zn	Si C	

While the invention has been described in detail with reference to certain specific embodiments, various changes and modifications which fall within the spirit of the invention and scope of the appended claims will become apparent to the skilled artisan. The invention therefore is only intended to be limited by the appended claims or their equivalents, wherein we have endeavored to claim all inherent novelty.

We claim:

1. A flame spray material comprising a composite in a form suitable for flame spraying, formed of at least two metal components which exothermically react with each other when melted, forming an intermetallic compound and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

2. A flame spray material comprising a composite in a form suitable for flame spraying formed of at least two metal components which exothermically react with each other when melted, forming an intermetallic compound with the release of at least 3,000 gram calories per gram atom and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

3. A flame spray material comprising a composite in a form suitable for flame spraying formed of at least two metal components which exothermically react with each other when melted, forming an intermetallic compound with the release of at least 7,500 gram calories per gram atom and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

4. A flame spray material comprising a composite in a form suitable for flame spraying formed of aluminum and nickel and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

5. Composite according to claim 4 in which said aluminum is present in amount of about 10–45%, based on the total of nickel and aluminum.

6. Composite according to claim 1 in which said components are component pairs selected from the group listed in Table I above.

7. A flame spray powder in the form of individual clad particles comprising a metal nucleus and at least one coating layer of a metal differing from said nucleus and exothermically reactive therewith when melted together, forming an intermetallic compound and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

8. A flame spray powder in the form of individual clad particles comprising a metal nucleus and at least one coating layer of a metal differing from said nucleus and exothermically reactive therewith when melted together, forming an intermetallic compound, with the release of at least 3,000 gram calories per gram atom and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

9. A flame spray powder in the form of individual clad particles comprising a metal nucleus and at least one coating layer of a metal differing from said nucleus and exothermically reactive therewith when melted together, forming an intermetallic compound, with the release of at least 7,500 gram calories per gram atom and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

10. A flame spray powder according to claim 7 in which said metal nucleus and metal differing from said nucleus are component pairs selected from the group listed in Table I above.

11. A flame spray powder according to claim 7 in which said coating layer is in the form of a finely divided metal powder bound to the nucleus by a binder.

12. A flame spray powder in the form of individual clad particles comprising a nucleus of aluminum and a coating layer of nickel and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

13. Powder according to claim 12 in which said aluminum is present in amounts of about 10–45% based on the total of nickel and aluminum.

14. A flame spray powder in the form of individual clad particles comprising a nucleus of nickel and a coating layer of finely divided aluminum particles bound to the nucleus with a binder and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

15. A non-cavitating flame spray wire comprising two separate metal components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

16. A non-cavitating flame spray wire comprising two separate metal components differing from each other and capable of exothermically reacting with each other when

melted together, forming an intermetallic compound, with the release of at least 7,500 gram calories per gram atom and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

17. A non-cavitating flame spray wire comprising two separate metal components differing from each other and capable of exothermically reacting with each other when melted together, one of said components being aluminum and the other nickel and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

18. A flame spray wire comprising two separate metal components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound, with the release of 7,500 gram calories per gram atom, said components being component pairs selected from the group listed in Table I above and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

19. A flame spray wire comprising a sheath of a first metal component and a powder core of at least one second metal component, said first and second components being capable of exothermically reacting with each other when melted together, with the release of at least 7,500 gram calories per gram atom and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

20. A flame spray wire according to claim 19 in which said sheath is aluminum and said core a mixture of aluminum and nickel powder.

21. A flame spray wire comprising individual strands of two separate metal components differing from each other and capable of exothermically reacting with each other when melted together, forming an intermetallic compound, with the release of at least 7,500 gram calories per gram atom and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

22. Flame spray material according to claim 1 additionally containing a metal hydride.

23. Flame spray material according to claim 1 in which one of the said components is at least partially in the form of a hydride.

24. Flame spray material according to claim 1 additionally containing a member selected from the group consisting of boron, silicon and mixtures thereof.

25. A flame spray material comprising a composite in a form suitable for flame spraying formed of at least two metal components which exothermically react with each other when melted, said components being component pairs selected from the group consisting of Al Co, Al Cr, Al Mo, Al W, Al Ta, Al Nb, Al Ti, Al Ni, Si Nb, Si Cr, Si W, Si Co, Si Mo, Si Ni, and Si Ta and characterized by the ability of generating heat during flame spraying which aids in bonding to the surface being sprayed.

26. A flame spray material according to claim 25 in the form of a powder.

27. A flame spray material according to claim 25 in which one of the components is in the form of a coating on the other component.

28. A flame spray material according to claim 25 in the form of a wire.

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April 1, 1969 F. J. DITTRICH ET AL 3,436,248

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Original Filed March 25, 1965

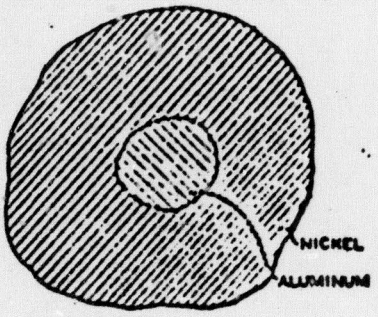

Fig. 1

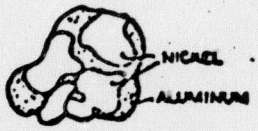

Fig. 2

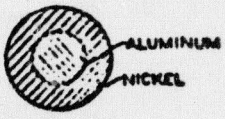

Fig. 3

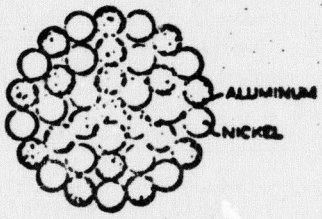

Fig. 4

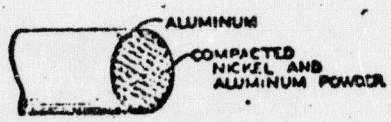

Fig. 5

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,436,248 April 1, 1969

Ferdinand J. Dittrich et al.

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 9, line 38, "Al-Nn" should read -- Al-Ni --. Column 13, line 56, "poyder" should read -- powder --. Column 14, line 20, "end" should read -- and --. Column 15, line 32, "Ce Mg" should read -- Ge Mg --; line 33, "Ce Nb" should read -- Ge Nb --; line 34, "Ce Zr" should read -- Ge Zr --. Column 18, line 24, "Mackin et al." should read -- Mackiw et al. --.

Signed and sealed this 7th day of April 1970.

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents

E 902

United States Patent Office

3,436,248

Patented Apr. 1, 1969

3,436,248

FLAME SPRAYING EXOTHERMICALLY REACTING INTERMETALLIC COMPOUND FORMING COMPOSITES

Ferdinand J. Dittrich, Bellmore, and Arthur P. Shepard, Flushing, N.Y., assignors to Metco, Inc., a corporation of New Jersey

Application Mar. 25, 1965, Ser. No. 442,727, now Patent No. 3,322,515, dated June 30, 1967, which is a continuation-in-part of application Ser. No. 343,705, Feb. 10, 1964. Divided and this application May 26, 1966, Ser. No. 592,238

Int. Cl. C23c 7/00, 13/02

U.S. Cl. 117—105

27 Claims

ABSTRACT OF THE DISCLOSURE

Method of coating a surface by flame spraying two or more components which will react with one another during the flame spraying to form an intermetallic compound.

This is a division of application Ser. No. 442,727, filed Mar. 25, 1965, now Patent No. 3,322,515, which was a continuation-in-part of applications, Ser. No. 72,543, filed Nov. 22, 1960, now abandoned; Ser. No. 134,544, filed Aug. 16, 1961, now Patent No. 3,254,970; Ser. No. 237,786, filed Oct. 26, 1962, now abandoned; and Ser. No. 343,705, filed Feb. 10, 1964, now abandoned.

This invention relates to the flame spraying of exothermically reacting intermetallic compound forming composites. The invention more particularly relates to the flame spraying of flame spray materials in the form of composites containing two or more components which will exothermically react with each other during the spraying, forming one or more intermetallic compounds, and to a novel group of such composites including powders and wires.

Flame spraying involves the feeding of a heat fusible material into a heating zone, wherein the same is melted or at least heat-softened, and then propelled from the heating zone in a finely divided form, generally onto a surface to be coated.

The material being sprayed is generally fed into the heating zone in the form of either a powder or a wire (the latter term designating both rods and wires). The spraying is effected in a device known as a heat-fusible material spray gun or a flame spray gun.

In the wire type flame spray gun the rod or wire of the material to be sprayed is fed into the heating zone formed by a flame of some type, where it is melted or at least heat-softened and atomized, usually by blast gas, and thence propelled in finely divided form onto the surface to be coated. The rod or wire may be a conventionally formed rod or wire of a metal, or may be formed by sintering together finely divided material, or by bonding together finely divided material by means of a plastic binder or other suitable binder which disintegrates in the heat of the heating zone, thereby releasing the material to be sprayed in finely divided form.

For spraying finely divided, i.e., powdered material, a powder type flame spray gun is used in which the powder, usually entrained in a carrier gas, is fed into the heating zone of the gun formed by a flame of some type. The powder is either melted or at least the surface of the grains heat-softened in this zone, and the thus thermally conditioned particles propelled onto a surface to provide a coating. In the powder type spray gun as no "atomizing" energy is required, a separate blast gas is often dispensed with, though the same may be supplied in order to aid in accelerating the particles and propelling them toward the surface to be coated.

The blast gas may be provided for both the wire type and powder type guns to perform the additional function of cooling the workpiece and the coating being formed thereon.

The heat for the heating zone is most commonly produced from a flame caused by the combustion of a fuel, such as acetylene, propane, natural gas, or the like, using oxygen or air as the oxidizing agent. The heat may, however, also be produced by an electrical arc flame or, in the newer type of guns, by a plasma flame. The plasma flame may in itself constitute part of an electric arc, or, in accordance with a newer development, may be in the form of a "free plasma stream," i.e., a stream of plasma which may be considered independent of the arc as it does not contribute to the electric flow between electrodes.

Heat-fusible material spray guns utilizing electric resistance heating or induction heating as the heat source have also been proposed but have not proven commercially successful except in connection with the spraying of low melting point metals, such as solders, lead and zinc.

Flame spraying in the initial stages of its commercial development was used mostly for the spraying of various metals and was often referred to as metallizing. However, the art of flame spraying extends to the spraying of a much wider group of materials, including higher melting point or refractory metals, ceramics, cermets, and the like, and such materials are of increasing commercial interest.

In the case of spraying heat-fusible materials in the initial form of a rod or wire, the rod or wire is generally of a single composition, i.e., in the form of a specific metal, alloy, ceramic, or the like. While it is true that rods or wires formed from finely divided material bound together with a binder of plastic or the like, as mentioned above, were known, the binder generally did not take part in the spraying or contribute to the coating, and merely served the purpose of maintaining the rod or wire in shape until fed into the heating zone.

In the case of flame spray powders, while powders formed of several constituents were known, the same were generally in the form of a powder mixture of the individual constituents or, at best, a particle aggregate.

One object of this invention is the spraying of the heat-fusible material in a novel form which allows the obtaining of superior results.

A further object of this invention is a novel group of flame spray materials.

These and still further objects will become apparent from the following description read in conjunction with the drawing in which:

FIG. 1 diagrammatically shows a cross-section of a grain of novel powder in accordance with the invention;

FIG. 2 is a cross-section of a further embodiment of an aggregate grain of novel flame spray powder in accordance with the invention;

FIG. 3 is a diagrammatic cross-section of an embodiment of a novel flame spray wire in accordance with the invention;

FIG. 4 shows a cross-section of a further embodiment of a novel flame spray wire in accordance with the invention; and

FIG. 5 shows a still further embodiment of a novel flame spray wire in accordance with the invention.

In accordance with the invention, the flame spraying is effected with the heat-fusible material in the form of a composite containing at least two components which will exothermically react with each other at the temperatures developed during the spraying, forming an intermetallic compound.

The term "composite" as used herein is intended to designate a structurally integral unit and does not include a mere mixture of components which may be physically

separated without any destruction of the structure. Thus, in the case of powder, the term "composite" does not include a simple mixture of individual granules of the separate components, but requires that each of the individual granules contain the separate components which will exothermically react, forming intermetallic compounds. In the case of wire, the individual components must be incorporated in a single wire. In the composite the components must be in intimate contact with each other.

In connection with powders, each grain may consist of an aggregate containing the two components which will exothermically react, forming the intermetallic compound, but preferably the individual grains of the powder are in the form of a clad composite consisting of a nucleus of one of the components and at least one coating layer of the other component. Alternatively, the composite may consist of separate, concentric coating layers of the two components and a nucleus of still a third material.

In the case of wires, the composites may be in the form of a wire having a coating sheath of one material and a core of the other, alternate coating sheaths of the components and a core of a third material, a wire formed by twisting or rolling separate wire strands of the components, a wire consisting of a sheath of one component and a core containing the other component in powder or compacted form, a wire consisting of a sheath of one component and a core containing a compacted powder mixture of this same component material and one or more other components, a wire consisting of a plastic sheath and a core containing a compacted powder mixture of components, etc.

In order for the wires to be satisfactory for spraying, the same must not cavitate at the tip when heated, and should preferably be capable of forming a pointed or slightly tapered tip when being melted and sprayed. Thus, if the wires have an outer layer or sheath of one component and an inner core of another component, the inner core cannot have a lower melting point than the outer sheath, as otherwise the inner core will initially melt, causing cavitation at the tip. For example, if the wire is composed of nickel and aluminum as the exothermically reacting components and is in the form of a core with a coating sheath, the core must be nickel and the coating sheath aluminum, as otherwise during the spraying the core will initially melt out, causing the cavitation which will interfere with a satisfactory spraying operation. The wire having the melting-point characteristics so as to allow the melting off of the tip without this cavitation, is referred to herein and in the claims as "non-cavitating wire."

As the components, any two metallics which may be melted together to form an intermetallic compound in an exothermic reaction may be used. The components should release about 3000 calories per gram atom, and preferably at least 7500 calories per gram atom in the exothermic reaction forming the intermetallic compounds. The term "calories per gram atom" as used herein denotes the number of gram calories which the average atomic weight in grams of the intermetallic compound formed will generate in so being formed. While the components are preferably present in the stoichiometric proportions required for the formation of the intermetallic compound, it is, however, possible to also have an excess of one or the other provided the relative amounts are sufficient to release the quantities of heat indicated above in the formation of the intermetallic compounds.

An extremely large number of metal components are known which can be melted together in an exothermic reaction, forming an intermetallic compound with the generation of heat. Any of these component pairs may be utilized in accordance with the invention, it only being required that the same be capable of being initially formed into the composite suitable for spraying and that the intermetallic compounds formed therefrom liberate the required amount of heat in the intermetallic compounds formation and are suitable as components of a sprayed coating. As a general rule, components which will form intermetallic compounds having a higher melting point will liberate sufficient heat to be useful in accordance with the invention. In certain instances, however, components which will form intermetallic compounds which do not have as high a melting point, will also liberate sufficient heat in the exothermic reaction and thus be useful. Preferred components are aluminum with one of Co, Cr, Mo, W, Ta, Nb, Ti, or most preferably Ni or silicon with at least one of Ti, Nb, Cr, W, Co, Mo, Ni or Ta.

While iron itself is not a satisfactory component, the same may be present in addition to another component, which in itself is satisfactory, such as in the form of an alloy therewith. This other component, however, must be present in amount sufficient to form the intermetallic compound with the other component of the composite, with the generation of sufficient heat to aid the spraying operation. Thus, for example, iron which just contains enough alloyed nickel to render the same rust-resistant, does not contain enough nickel for an effective exothermic reaction with aluminum. Generally an alloy of nickel and iron must contain at least about 12% nickel for this purpose.

FIG. 1 shows a composite powder consisting of a nucleus of aluminum and a coating layer of nickel. FIG. 2 shows an aggregate of these components and FIGS. 3, 4 and 5 show various forms of wire containing these components. FIG. 3 showing a wire having an aluminum core with a nickel sheath. FIG. 4 showing a wire made of alternate strands of nickel and aluminum wire, as for example 18 strands of 25 gauge (.019" diameter) nickel wire marked 1, and 19 strands of 25 gauge aluminum wire marked 2; and FIG. 5 shows a sheath of aluminum filled with granules of nickel and aluminum.

Where one of the component metals is available as a metal hydride, the same may be used in this form rather than as a metal per se. When flame sprayed the hydrogen gas evolved from the hydride produces a reducing atmosphere, which in turn suppresses oxidation of the intermetallic compounds during and immediately after their formation. Thus, for example, in place of titanium, titanium hydride may be used as one of the components.

Also for the purpose of reducing oxidation a metal hydride, such as titanium hydride, may be added in a minor amount to the other components. This, for example, 1–10% by weight, and preferably 1–5% by weight, based on the total of the hydride and other components, may be used.

In addition, the powder granules and the wire may contain other conventional flame spray components, or be sprayed in admixture or in conjunction therewith. Thus, for example, the coated powders may additionally contain other coating layers of other flame spray components or may contain a nucleus of another flame spray material with alternate coating layers of the components which will exothermically react, forming the intermetallic. In a similar manner, the aggregates or the wires may contain further flame spray components, and in the case of powders, the same may additionally be admixed with any other desired flame spray powder.

The clad powders, in accordance with the invention, may be formed in any known or desired manner, and preferably by the known chemical plating processes in which coating material is deposited on a seed or nucleus of the other material, or in which multiple layers of various materials are built up on the seed material, or in which various materials are co-deposited in a single layer on the seed material.

A mode of forming the clad powders involves the depositing of a metal from a solution by reduction on a seed or nucleus, such as by the hydrogen reduction of ammoniacal solutions of nickel and ammonium sulfate on a seed powder catalyzed by the addition of another compound. It is also possible to form the coating by the use of other known coating processes, such as coating by vapor de-

position, by the thermal decomposition of metal carbonyls, by hydrogen reduction of metal halide vapors, by thermal deposition of halides, hydrides, carbonyls, organo metals, or other volatile compounds, or by displacement gas plating or the like.

A preferred and greatly simplified mode of forming the clad powders in accordance with the invention is the depositing of one component as a coating in the form of a paint on the other component. Thus, one of the components which is to form the coating or cladding, may be dispersed in finely divided form in a binder or lacquer so as, in effect, to form a paint in which this component corresponds to the pigment. The paint is then used to coat core particles of the other component and the binder or lacquer allowed to set or dry. The binder material is preferably a resin which does not depend on solvent evaporation in order to form a dried or set film, and which film will decompose or break down in the heat of the spraying process. The binder, for example, may be a phenolic varnish or any other known or conventional varnish, preferably containing a resin as the varnish solids. The component which is initially mixed with the binder or varnish should preferably be as finely divided as possible, as for example —325 mesh. The other component which constitutes the core should be approximately or only slightly below the particle size ultimately desired for the spray powder. The coating of the core component with the "paint" may be effected in any known or desired manner, and it is simply necessary to mix the two materials together and allow the binder to dry or set, which will result in a fairly free-flowing powder consisting of the core component coated with a cladding of the other component bound in the binder.

The aggregates may be formed by compacting or briquetting the various components into the individual granules, or into larger aggregates and then breaking these aggregates into the granules.

The wires may be formed in the known conventional manner for forming wires with various components as, for example, by shrinking a sheath on a core, by forming the core with powder, by twisting the component wires, followed by rolling, drawing, swaging, or the like if desired.

In accordance with one mode of manufacture, one of the components may be formed into a tube or sheath and filled with a powder of the other component or a powder comprising a mixture of the two components, or containing additional components. The tube ends are then sealed and the wire reduced to the desired wire diameter by swaging, rolling or drawing. Preferably the powder or powder mixture is first compressed into cylindrical briquettes before being placed in the sheath or core. The sealing of the tube ends after loading with the powder or powder mixture can be effected, for instance, by insertion of a plug, for example of the metal of the sheath, by welding, twisting, crimping, or the like.

Powders in accordance with the invention should have the general over-all shape and size of conventional, flame-spray powders, and thus for example should have a size between —60 mesh and +3 microns and preferably —140 mesh and +10 microns (U.S. Standard screen mesh size). Most preferably the powder should be as uniform as possible in grain size, with the individual grains not varying by more than 250 microns and preferably 75 microns.

Depending on the particular flame spray process and the desired purpose, the composite powders may be sprayed per se or in combination with other different composite powders, or in combination with other conventional flame spray powders or powder components.

While the powders are preferably sprayed, as such, in a powder-type of flame spray gun, it is also possible to combine the same in the form of a wire or rod, using a plastic or similar binder, which decomposes in the heating zone of the gun, or in certain cases the powders may be compacted and/or sintered together in the form of a rod or wire. The wires must have the conventional sizes and accuracy tolerances for flame spray wires, and thus for example may vary in size between ⅛" and 20 gauge, and are preferably of the following sizes: 3/16" +.0005", —.0025", ¼" +.0005", —.0025", 11 gauge —.0005", —.0025", and 15 gauge +.001", with a smooth, clean finish free from surface marks, blemishes, or defects. The wires are sprayed in the conventional manner, using conventional wire-type flame spray guns.

In combining, in the exothermic reaction, forming the intermetallic compound, the components generate heat in situ in the actual material which is to form at least a part of the coating. This is to be distinguished from flame-spray processes and materials in which heat is generated by a reaction, such as an oxidation reaction, in which a foreign and non-metallic element is introduced and in which undesirable components may be produced. Aside from greatly contributing to the thermal efficiency of the process, the heat generated in situ in the formation of the intermetallic compound produces novel results, in many instances forming a denser, more adhering coating, having characteristics of at least a partially fused coating. In many instances the coating has self-bonding characteristics, so that special surface preparation, other than a good cleaning, is not required. The spraying in all other respects is effected in the conventional, well-known manner, using conventional flame spray equipment, and the conventional surface preparation may be utilized, if desired. The composites in accordance with the invention may be sprayed in conjunction with, or in addition to, other flame spray materials conventionally used in the art, or may be sprayed in combination or conjunction with the others.

The use of the composites as, for example, the nickel-aluminum composites, will generally improve the bond of the total sprayed material, and thus of the other component or components to the substrate, sometimes making the mixture self-bonding. The particle bond will be improved and the coating will be denser, so that its porosity may be decreased. In general, as little as 10% by weight of the composites in accordance with the invention will be sufficient to substantially improve the bonding characteristics and decrease the porosity of other flame spray materials, such as conventional flame spray metals, alloys or ceramics. There is, of course, no upper limit on the amount, as the composite may be sprayed per se, but generally at least about 20% by weight of the other component is required if this component is to have a pronounced effect on the characteristics of the coating.

The following examples are given by way of illustration and not limitation:

Example I

(a) An aluminum powder having a particle size between —140 mesh and +325 mesh (U.S. Standard screen size) is coated with nickel in the known manner by the hydrogen reduction of an ammoniacal solution of nickel and ammonium sulphate, using anthraquinone as the coating catalyst. The reduction is effected at a temperature between about 300 and 350° F. in a mechanically agitated autoclave using solutions containing 40–80 grams per liter of nickel and 10–30 grams per liter of $(NH_4)_2SO_4$ and 20–30 grams per liter of NH_4. About .2 gram per liter of anthraquinone is used as the catalyst and the autoclave is pressurized with hydrogen at a pressure of about 300 lbs. p.s.i.g. After the nickel solution is depleted and the aluminum coated with an initial coating of nickel, the solution is discharged from the autoclave and replenished with a fresh solution which need not contain further amounts of the anthraquinone coating catalyst, as the initially formed nickel coating in itself acts as a catalyst. The cycle is continuously repeated until a composite powder is formed containing about 16 to 18% by weight aluminum and 84 to 82% by weight of nickel, and a size of —100 to +270 mesh.

The powder thus formed is flame-sprayed on a mild steel plate which has been surface-cleaned with emery cloth. The spraying is effected at about 9 inches from the plate, using a powder type flame-spray gun as described in U.S. Patent 2,961,338, issued Nov. 22, 1960 and sold by Metco Inc. of Westbury, Long Island, under the trade name of "Thermo-spray" powder gun. The spraying is effected at a rate of 6 to 9 lbs. of powder per hour, using acetylene gas as the fuel at a pressure of 10 p.s.i. and a flow rate of 17 to 25 cu. ft./hr. and oxygen as the oxidizing gas at a pressure of 12 p.s.i. and a flow rate of 29 to 35 cu. ft./hr.

The nickel coating and the aluminum base combine in the heat of the flame with a strong exothermic action, forming a mixture of nickel aluminum intermetallic compounds which deposit on the base as a dense, high quality coating which exhibits self-bonding characteristics. A coating layer of .002"–.004" thickness is built up in this manner. The coating may be used as a base material for spraying of further layers of different metals or the like, and serves as an excellent intermediate bonding layer.

The coating layer may also be built up to a greater thickness as, for example, .010"–.020", for use as an oxygen barrier undercoat, or to even greater thickness as, for example, .020"–.040" or thicker as a wear-resistant-oxidation-resistant surface.

Due to its self-bonding characteristics the sprayed coating will adhere to a base without the conventional surface preparation or roughening, and due to the natural characteristics of a sprayed material, will allow further materials to be sprayed thereon with good bonding. The coating formed from the powder has excellent oxidation-resistant characteristics even at high temperatures and in oxidizing atmospheres, and will for example prevent the oxidation of base materials, such as molybdenum or the like. The sprayed coatings may be used as a lining in metal-melting crucibles or molten metal-handling equipment, and will not be wetted or penetrated by many molten metals, including self-fluxing alloys. Coatings formed of the sprayed material also show good potential as high temperature, wear-resistant coatings.

When the example is repeated on a molybdenum rod of ¾" diameter, with a coating between .010"–.012" thick, the coated rod may be repeatedly heated to approximately 2000° F. in air, in an electric furnace and cooled to room temperature with no visible oxidation occurring.

Similar results may also be obtained if the composite powder contains 10–45% by weight of aluminum and 55–90% by weight of nickel.

(b) Example 1(a) is repeated, using, however, cobalt in place of the nickel. Comparable results are obtained.

(c) Example 1(a) is repeated, using titanium hydride (TiH_2) powder in place of the aluminum and in an amount of 25–85 weight percent, and preferably 60–85 weight percent of the total. The coating formed upon spraying is hard and dense, and when sprayed on a smooth, pressed and sintered Al_2O_3 substrate, an excellent bond is formed. The spraying may be effected with an oxygen-hydrogen or oxygen-acetylene flame.

Example 2

Example 1 is repeated with the spraying being effected in turn on the following bases and prepared in the following manner:

Low alloy steels and stainless steels, smooth-ground to remove surface contamination; copper and copper base alloys, rough-ground or light-grit-blasted; aluminum and aluminum base alloys, rough-ground or light-grit-blasted; magnesium, rough-ground or light-grit-blasted; and titanium, rough-ground or light-grit-blasted.

In each case when a further material, such as steel, alumina or the like, was sprayed over the coating in the conventional and well known manner, the same was bonded with a tenacious bond, though if this material had been initially sprayed on the surface as prepared in the manner indicated above, a satisfactory bond would not be obtained.

Example 3

The nickel-clad powder of Example 1 is mixed with an Al_2O_3 powder having a particle size between 62 microns and 10 microns, in the ratio of about 40% of the nickel-clad powder with 60% by weight of the ceramic. The powder is sprayed, using the gun described in Example 1, on a mild steel plate which has been surface-cleaned by smooth grinding. Spraying is effected at a distance of about 9" from the plate at a rate of about 4 to 8 lbs. of powder per hr., using acetylene at a pressure of 10 lbs. p.s.i. and a flow rate of 17–25 cu. ft./hr., and oxygen at a pressure of 12 p.s.i. and a flow rate of 29–35 cu. ft./hr.

A self-bonding cermet coating is formed which showed excellent thermal shock-resistance, hardness, abrasion-resistance, and which strongly inhibited oxidation of the base.

It is possible to vary the percentages of the ceramic in the mixture between 5 and 85% in order to vary the properties of the coating. With an increased amount of the intermetallic compound in the cermet coating formed, the bonding and thermal shock-resistant properties increased, whereas with an increased amount of the ceramic, the hardness and wear-resistant properties of the coating are increased and the thermal conductivity decreased.

Example 4

Example 3 is repeated, using the following materials in place of the aluminum oxide:

Zirconia, calcium zirconate, magnesium zirconate, spinel, ceria oxide, hafnium oxide, rare earth oxides, molybdenum disilicide, tungsten silicide, chromium silicide, titanium silicide, tungsten carbide, titanium carbide and chromium carbide.

In each case an excellent coating was formed.

Example 5

A nucleus of silicon powder is coated with nickel to form a nickel-clad flame spray powder having a particle size between 100 and 325 mesh and containing 75–85% nickel based on the silicon-nickel total. The composite powder is sprayed with the flame spray gun described in Example 1 on a steel base prepared by lightly grit-blasting, using the spraying conditions as described in Example 1. During the spraying silicon combines with the nickel in an exothermic reaction, greatly enhancing the thermal efficiency of the spraying and producing an excellent coating.

Example 6

Titanium is coated with nickel as described in Example 1 to produce a powder having a particle size between 100 and 325 mesh and containing 10 to 50% nickel based on the titanium-nickel total.

The nickel protects the titanium from oxidation during storage and when spraying.

Upon spraying in the manner described in Example 1, on a base material prepared by grit blasting, the nickel and titanium combine exothermically in the flame to form a corrosion-resistant coating comprising a nickel-titanium intermetallic compound.

Example 7

Tellurium powder was coated with copper so as to form a composite having a particle size between 100 and 325 mesh and containing 30 to 70% copper based on the tellurium-copper total.

Upon spraying in the manner described in Example 1, on a base material prepared by grit-blasting, the copper and tellurium combine to form a new material.

During the spraying heat was evolved upon the combination of the copper and tellurium, increasing the thermal economy of the process.

Example 8

The nickel-clad flame spray powder of Example 1 is mixed with about 20% by weight of low pressure polyethylene powder and molded at a temperature of about 212° F. into the form of a rod of ¼" diameter. The rod is sprayed, using a conventional wire-type flame spray gun sold by Metco Inc. of Westbury, Long Island, as the Metco-type 4-E gun. The spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu. ft./hr. with oxygen as oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu. ft./hr.; with air as a blast gas at a pressure of 40 p.s.i. and a flow rate of 25 cu. ft./min. The end coating produced is similar to the coating produced in Example 1.

Example 9

A wire is formed by encasing a core of nickel in a tube of aluminum and drawing to a size of .125" in diameter plus or minus .002". The wire contains 82 to 84% by weight of nickel based on the aluminum-nickel total.

The wire is sprayed, using a conventional wire type flame spray gun sold by Metco Inc. of Westbury, Long Island, as the Metco-type 4-E gun. Spraying is effected with acetylene at a pressure of 15 p.s.i. and a flow rate of 37 cu. ft./hr. with oxygen as the oxidizing gas at a pressure of 38 p.s.i. and a flow rate of 75 cu. ft./hr. Air is used as a blast gas at a pressure of 55 p.s.i. and a flow rate of 30 cu. ft./min. The end coating produced is similar to the coating produced in Example 1.

Similar results are also obtained using 55-90% by weight of nickel in the wire.

Example 10

A composite wire is formed by winding individual wires of nickel and aluminum to form a stranded wire with a diameter of .125" plus or minus .002". The wire contains 55 to 90% by weight of nickel based on the total Al-Ni. The wire is sprayed in the manner described in Example 9, with identical conditions and coating resulting.

Example 11

A silicon powder having a particle size between 140 and 325 mesh is coated with molybdenum in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The molybdenum coating and the silicon base combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

Example 12

A molybdenum powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 39% by weight of silicon and about 61 to 65% by weight of molybdenum, and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of type 2MB plasma flame gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using a mixture of argon and hydrogen gas as the plasma gas, with argon at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., and hydrogen at 50 p.s.i. and a flow rate of 25 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu. ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57-62 volts.

The molybdenum base and silicon coating combine in the heat of the flame, forming a molybdenum silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

Example 13

A silicon powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The chromium coating and the silicon base combine in the heat of the flame, forming a chromium-silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at elevated temperatures and will protect the base material from oxidation.

Example 14

A chromium powder having a particle size between 140 and 325 mesh is coated with silicon in the known manner, and a composite powder is formed containing about 48 to 85% chromium and 15 to 52% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the tradename of Type 2MB plasma flame gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu.ft./hr., using a standard electrode and "D" Argon nozzle, and using arc current of 400-500 amperes at 57-62 volts.

The chromium base and silicon coating combine in the heat of the flame, forming a chromium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

Example 15

A zirconium powder having a particle size between 140 and 325 mesh is coated with chromium in the known manner and a composite powder is formed containing about 45% zirconium and 55% chromium by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material in the manner described in Example 1.

The chromium coating and the zirconium base combine in the heat of the flame, forming a chromium zirconium intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures.

Example 16

A titanium powder having a particle size range between 140 and 325 mesh is coated with silicon in the known manner and a composite powder is formed containing about 35 to 65% titanium and 35 to 65% silicon by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting. The spraying is effected at about five inches from the

plate, using a powder type plasma flame-spray gun sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of Type 2MB plasma flame gun. The spraying is effected at a rate of six to nine lbs. of powder per hour, using argon gas as the plasma gas at a pressure of 100 p.s.i. and a flow rate of 110 cu. ft./hr., using argon as the powder carrier gas at 100 p.s.i. and a flow rate of 15 cu. ft./hr., using a standard electrode and "1" Argon nozzle, and using arc current of 400-500 amperes at 57-62 volts.

The titanium base and silicon coating combine exothermically in the heat of the flame, forming a titanium silicon intermetallic which deposits on the base as a dense, high quality coating which exhibits excellent resistance to oxidation at high temperatures and will protect the base material from oxidation.

Example 17

A dysporsium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 60 to 75% dysprosium and 25 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by light grit-blasting in the manner described in Example 1.

The aluminum coating and the dysprosium base combine in the heat of the flame with a strong exothermic action, forming a dysprosium aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

Example 18

A lanthanum powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed containing 70 to 75% lanthanum and 25 to 30% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the lanthanum base combine exothermically in the heat of the flame with a strong exothermic action, forming a lanthanum aluminum intermetallic compound which deposits on the base as a dense, high quality coating which exhibits excellent properties at high temperatures.

Example 19

A chromium powder having a particle size between 140 and 325 mesh is coated with aluminum in the known manner and a composite powder is formed consisting of 60 to 62% chromium and 38 to 40% aluminum by weight and a size of 100 to 270 mesh.

The powder thus formed is flame-sprayed on a base material which has been prepared by grit-blasting in the manner described in Example 1.

The aluminum coating and the chromium base combine in the heat of the flame with a strong exothermic action, forming a chromium aluminum intermetallic compound which deposits on the base as a dense, high quality coating of very high melting point and excellent oxidation-resistance.

Example 20

Example 19 is repeated except that the composite powder is formed with an aluminum core and chromium coating. Identical results are obtained.

Example 21

The nickel-clad aluminum composite powder of Example 1 is mixed with cobalt bonded tungsten carbide particle powder having a particle size range of −140 mesh +10 microns, and preferably −140 +325 mesh in proportions of:

(a) 80 weight percent tungsten carbide to 20 weight percent of the composite.

(b) 20 weight percent of the carbide to 80 weight percent of the composite, and

(c) preferably 50 weight percent each of the tungsten carbide and composite.

The powder mixtures are each flame-sprayed on a mild steel plate which has been surface-cleaned by machining or very light sand-blast cleaning. The spraying is effected at about 8-9 inches from the plate, using a powder-type flame-spray gun as described in U.S. Patent 2,961,335 issued Nov. 22, 1960, and sold by Metco Inc. of Westbury, Long Island, New York, under the trade name of "Thermo-Spray" powder gun. The spraying is effected at a rate of 6 to 10 lbs. per hour using acetylene gas as the fuel at a pressure of 12 p.s.i. and a flow rate of 20 to 30 cu. ft./hr. and oxygen as the oxidizing gas at a pressure of 14 p.s.i. and a flow rate of 30 to 40 cu. ft. hr.

The nickle-aluminum composite powder in the mixture reacts exothermically in the flame to provide the self-bonding properties of the mixture and, being fully molten on impact with the substrate, becomes the matrix which securely binds the tungsten carbide particles together in the coating.

Used as sprayed, or finished by proper grinding procedure, the resultant coating is of a highly wear-resistant coating material, applicable to virtually any base material and not subject to the limitations of the previously used self-fluxing alloy matrix materials which must be fused at approximately 1900° F.

Example 22

Example 21 is repeated except that in place of the grade of tungsten carbide cobalt powder grains used, cobalt-bonded tungsten carbide grains with lower cobalt content and sharp, angular shape are used.

The powder was sprayed in the manner described in Example 21. The sharp, angular edges of the initial tungsten carbide particles were retained in the coating.

The deposited coating may be suitably finished by grinding for use as a wear-resistant coating or used as deposited where the coated article is to be used as a hone or lap, the sharp edges of the carbide inclusions constituting the abrading or cutting edges.

Example 23

Example 22 is repeated except that in place of the tungsten carbide grains described, cobalt-bonded tungsten carbide particles of sharp, angular shape were used which were first coated with nickel in the manner described in Example 1, so as to produce nickel-clad particles having a size between 100 and 325 mesh and containing from 20-50% nickel based on the tungsten carbide-nickel total.

Example 24

The nickel-clad aluminum composite described in Example 1 is mixed with a columbium (niobium) powder of size between −120 mesh and +10 microns and preferably −140 +325 mesh in the proportions of 60 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and when properly finished, by grinding or other means, is a highly wear-resistant, hard coating.

Example 25

The nickel-clad aluminum composite described in Example 1 is mixed with a molybdenum powder of a size between −120 mesh and +10 microns and preferably −140 +325 mesh in the proportions of 65 weight percent molybdenum to 35 weight percent of the nickel-aluminum composite.

The powder mixture is sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and when properly

finished, by grinding or other means, presents a highly wear-resistant, hard surface.

Example 26

Example 21 is repeated except in place of the tungsten carbide, other carbides such as titanium carbide, tantalum carbide, columbium carbide, chromium carbide and mixtures of the various carbides are used.

Example 27

The nickel-clad aluminum core composite from Example 21 is mixed with aluminum powder in the mesh size range −100 +325 mesh, and preferably in the −170 +325 mesh size range in the proportions of 80 weight percent nickel aluminum composite to 20 weight percent aluminum.

The mixture was sprayed in the manner described in Example 21. The coating as deposited consists of an intimate mixture of the flame-reacted nickel aluminide and aluminum securely bonded to the base and particle to particle within the coating.

Upon heat-treating in the temperature range 1250° F. to 1500° F. in reducing atmosphere, dry hydrogen for instance, the nickel aluminide and aluminum combine to form a dense, homogenous coating fused to the base material which can be used for "cathodic" protection of iron and steel subject to water and salt-water corrosion.

Example 28

The nickel-clad aluminum composite powder of Example 21 is mixed with Monel powder of a size between −100 mesh and +10 microns, and preferably between −140 and +325 mesh in the proportions 35 weight percent composite to 65 weight percent Monel.

The powder mixture was sprayed in the manner described in Example 21. The resultant coating is self-bonding to a wide variety of substrate materials and the inclusion of the nickel-aluminum composite, the components of which combine exothermically in the flame to provide the self-bonding ability of the mixture, considerably increase the particle to particle bonds within the coating and decrease the permeability of the coating.

Example 29

Example 28 is repeated except that nickel and stainless steel powders are substituted for the Monel.

Example 30

Example 28 is repeated except that chromium is substituted for the Monel.

The resultant coating when properly finished, by grinding or other means, shows high resistance to abrasion, wear, and galling by other metals, and is an excellent bearing surface.

Example 31

Finely divided aluminum powder (−325 mesh) was blended with a phenolic varnish having approximately 50% solid contents so as to form a mixture having the consistency of a heavy syrup and containing 60% by weight of the metallic aluminum.

100 grams of this varnish aluminum powder mixture was added to 240 grams of nickel powder having a size between −200 and +325 mesh, and the two were thoroughly mixed, with the mixing continued until the varnish dried, leaving a fairly free-flowing powder in which all of the nickel core particles were clad with a dry film, which consisted of aluminum particles bonded to each other and to the core material by the phenolic binder. The powder is then warmed to 250° F. to insure complete drying. There were some minor agglomerates which were screened out and hand-milled to reduce the same to a −100 mesh powder. The end powder consisted of approximately 15 weight percent aluminum and 85 weight percent nickel due to the loss of some aluminum during the milling. The powder is sprayed in the manner described in Example 1 producing a similar coating having, however, more than twice the tensile strength of the coating produced in Example 1.

Example 32

(a) A mixture of 6 weight percent aluminum and 94 weight percent nickel powder are thoroughly blended and pressed together in the form of cylindrical briquettes which are loaded into an aluminum tube of .375" outside diameter, after which the tube ends are welded closed. The ⅜" diameter feed stock is then swaged to ⅛" diameter, then to a 7/64" diameter and then to a 1/16" finished wire diameter. The wire is then annealed and coiled. The wire is then sprayed, using the conventional wire type flame spray gun sold by Metco Inc. as the Metco Type 4-E gun. Spraying is effected, using acetylene at a pressure of about 15 lbs. p.s.i. and a flow rate of 37 cu. ft. hr. and oxygen as the oxidizing gas at a pressure of 35 lbs. p.s.i. and flow rate of 75 cu. ft./hr. Air is used as a blast gas at a pressure of 55 lbs. p.s.i. and flow rate of 30 cu. ft./min. The wire is sprayed at a rate of 8 ft. per minute. The spray material is deposited on a surface of ground and machine-finished, cold rolled steel with a tensile bond strength of 3820 lbs. p.s.i. The sprayed coating is hard and dense; it is wear- and oxidation-resistant and it also could serve as a base for further spraying.

(b) Example 32(a) is repeated except that chromium is used in place of the nickel powder in amounts of from 24–95 weight percent, based on the total of the aluminum and chromium. Spraying results in a high quality coating which has self-bonding properties and is resistant to oxidation at high temperatures.

(c) Example 32(a) is repeated, using columbium powder in place of the nickel powder in amounts of from 40–90 and preferably 50–85 weight percent, based on the total of the columbium and aluminum. The sprayed coating formed is a high quality coating which is resistant to oxidation at high temperatures and may be used to protect tantalum and molybdenum bases from oxidation.

(d) Example 32(a) is repeated, using tantalum powder in place of the nickel powder in amounts of 40–90 weight percent and preferably 65–75 weight percent of tantalum, based on the total of tantalum and aluminum. The sprayed coating is a dense, high quality coating which is self-bonding and is resistant to oxidation at high temperatures.

(e) Example 32(a) is repeated, using boron powder in place of the nickel powder in amounts of 40–90 weight percent, based on the total of boron and aluminum. The resulting sprayed coating is self-bonding and is resistant to oxidation at high temperatures.

(f) Example 32(c) is repeated except that the powder additionally contains 0.5 to 5 weight percent of boron, and/or 0.5 to 5 weight percent of silicon, based on the total of the components. The coating formed is similar to that obtained in Example 32(c) except that on heating to high temperature in air, a very thin, dense, adherent, protective oxide film forms on the surface of the intermetallic compound formed, which is resistant to spalling due to thermal shock, and which is believed self-healing.

(g) Example 32(a) is repeated except that tungsten carbide containing 12% binder and having a particle size below −140 mesh is added in amount of 5–70 weight percent, based on the total of the components. The resulting coating is a dense, extremely wear-resistant coating, which has self-bounding properties. This example may be further repeated, using in place of the tungsten carbide specified, crystalline tungsten carbide, aluminum oxide, diamonds or any other abrasive material.

(h) Example 32(a) is repeated. However, 1–10% by weight and preferably 1–5% by weight of titanium hydride of a size below −100 mesh and preferably below −325 mesh, based on the total of the components, is added to the core material. The results are the same as indicated in Example 32(a) except that the coating formed is of im-

proved physical strength, containing considerably less oxide inclusions. In place of the titanium hydride other metal hydrides may be used.

(i) Example 32(a) is repeated except that the nickel powder is replaced with a nichrome powder consisting of a chrome alloy containing 80% nickel and 20% chromium. When sprayed the wire gives a dense, self-bounding coating which is extremely oxidation-resistant.

(j) Example 32(a) is repeated except that the nickel powder is replaced with a powder mixture consisting of 80% by weight nickel and 20% by weight chrome. When sprayed the wire gives a dense, self-bounding coating which is highly oxidation resistant.

Example 33

Table I below gives examples of further component pairs which may be used to form the powders and/or wires in accordance with the invention.

Each of the component pairs as listed in Table I below may be formed into a composite powder or wire as described above, and when flame-sprayed will exothermically react, forming an intermetallic compound and high grade coating. Thus, the component pairs may be formed into clad powders as described in Example 31 and sprayed as described therein, or formed into a composite wire as described in Example 32 and sprayed as described therein.

TABLE I

Ag Ce	Ga Pr
Al As	Ga Sb
Al Au	Ga Te
Al B	Ga U
Al Ba	Ce Mg
Al Ca	Ce Nb
Al Ce	Ce Zr
Al Co	H V
Al Cr	Li In
Al La	In Te
Al Li	In Ru
Al Mo	K Sb
Al Nb	K Se
Al Ni	K Sn
Al Pr	K Te
Al Ti	La Pb
Al Zr	La Sb
Al Sb	La Sn
Al Se	La Te
Al Ta	La Zn
Al Te	Li Pb
Al U	Li Sb
Al V	Li Sn
Al W	Li Tl
As Cd	Li Zn
As Ga	Mg Sb
As In	Mg Sn
As Mg	Na Pb
As Zn	Na Sb
B Y	Na Se
B C	Na Sn
B Cr	Na Te
B Hf	Na Tl
B Nb	Nb Si
B Ta	Ni Th
B Th	Pb Pr
B Ti	Pb Pu
B V	Pb Se
B W	Pb Tl
B Zr	Pd U
Ba Bi	Pr Sn
Ba Pb	Pr Tl
Ba Sb	Sb Zr
Be Co	Se Sn
Be Cr	Se Th
Be Ni	Se Tl
Be Np	Cu Te
Be Pu	Si Ti
Be U	Si U

TABLE I Continued

Be Zr	Si V
Bi Ca	Si Zr
Bi Ce	Sn Te
Bi K	Sn U
Bi Li	Sn Zr
Bi Mg	Te Zn
Bi Na	Mo Be
Bi Se	Nb Be
Bi Te	Ta Be
Bi Th	V Be
Ca Pb	Ti Be
Ca Sn	Cr Si
Ca Tl	Cr Ti
Cd Li	Cr Zr
Cd Na	Mg Te
Ce In	Ni Te
Ce Mg	Si Th
Ce Pb	Si W
Ce Si	Co Si
Ce Sn	Mo Si
Ce Tl	Ni Si
Ce Zn	Si Ta
Ga Na	

We claim:

1. In the flame spray process in which a heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in such condition out of said zone in finely divided form onto a substrate, the improvement which comprises passing the heat-fusible material into said zone in the form of a composite comprising at least two distinct components alloyed together as a single alloy and in proportion and form sufficient to exothermically react with each other at the temperature developed in the heating zone, forming an intermetallic compound.

2. Improvement according to claim 1 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.

3. Improvement according to claim 1 in which said components are components which exothermically react with each other, with the release of at least 7,500 gram calories per gram atom.

4. Improvement according to claim 1 in which one of said components is aluminum and the other nickel.

5. Improvement according to claim 4, in which said aluminum is present in amount of about 10 to 45% by weight, based on the total of nickel and aluminum.

6. Improvement according to claim 1 in which said components are component pairs selected from the group listed in Table I above.

7. Improvement according to claim 1 in which said composite contains at least one additional flame spray material.

8. Improvement according to claim 1 in which said composite is sprayed in conjunction with at least one further flame spray material.

9. In the flame spray process in which heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form onto a substrate, the improvement which comprises passing the heat-fusible material into said zones in the form of individual clad powder particles comprising a nucleus and a coating layer which will exothermically react with the nucleus at the temperature developed in the heating zone, forming an intermetallic compound.

10. Improvement according to claim 9 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.

11. Improvement according to claim 9 in which said components are components which exothermically react

with each other, with the release of at least 7,500 gram calories per gram atom.

12. Improvement according to claim 9 in which said nucleus is aluminum and said coating layer nickel.

13. Improvement according to claim 12 in which said aluminum is present in amount of about 10–45%, based on the total of nickel and aluminum.

14. Improvement according to claim 9 in which the nucleus and coating layers are selected from the members of the group consisting of the pairs listed in Table I.

15. Improvement according to claim 9 in which said coating layer consists of fine particles bound to said nucleus by a binder.

16. Improvement according to claim 9 in which said clad powder particles are in admixture with another flame spray powder.

17. In the flame spray process in which heat-fusible material is heated in a heating zone to at least heat-softened condition and propelled in said condition out of said zone in finely divided form onto a substrate, the improvement which comprises passing the heat-fusible material into said zone in the form of a composite, non-cavitating wire comprising at least two components which exothermically react with each other at the temperatures developed in the heating zone, forming an intermetallic compound.

18. Improvement according to claim 17 in which said components are components which exothermically react with each other, with the release of at least 3,000 gram calories per gram atom.

19. Improvement according to claim 17 in which said components are components which exothermically react with each other, with the release of at least 7,500 gram calories per gram atom.

20. Improvement according to claim 17 in which one of said components is aluminum and the other nickel.

21. Improvement according to claim 20 in which said aluminum is present in amount of about 10–45% by weight, based on the total of nickel and aluminum.

22. Improvement according to claim 17 in which said components are component pairs selected from the group listed in Table I above.

23. Improvement according to claim 17 in which said wire is in the form of a sheath of one component containing a powder of the other component, said sheath being of a component having a lower melting point than the other component.

24. Improvement according to claim 23 in which said sheath is an aluminum sheath and in which said core is a compacted mixture of aluminum and nickel powder.

25. Improvement according to claim 17 in which said wire is a multi-strand wire with individual strands of said components.

26. Improvement according to claim 1 in which the heat-fusible material additionally contains a metal hydride.

27. Process according to claim 47 in which one of said components is at least partially in the form of a hydride.

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ALFRED L. LEAVITT, *Primary Examiner.*

A. GALIAN, *Assistant Examiner.*

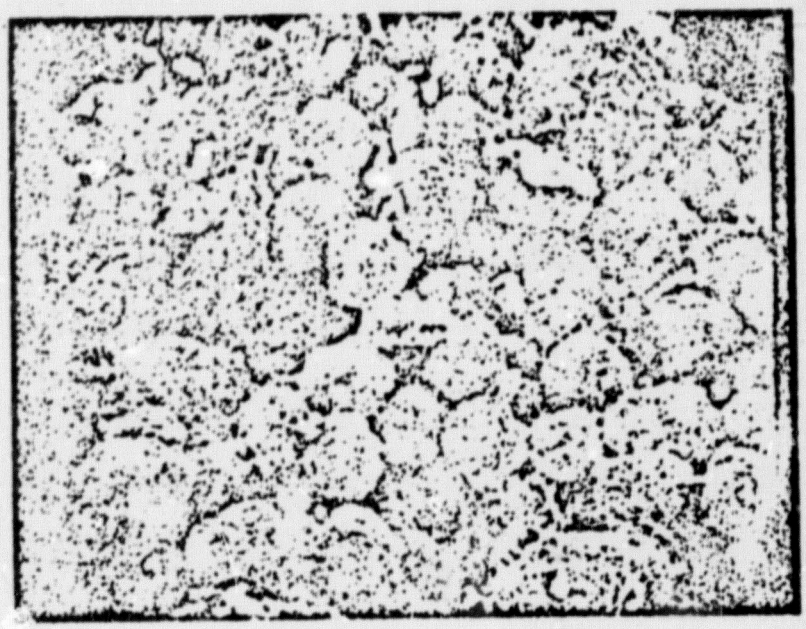
U.S. Cl. X.R.

117—105.2

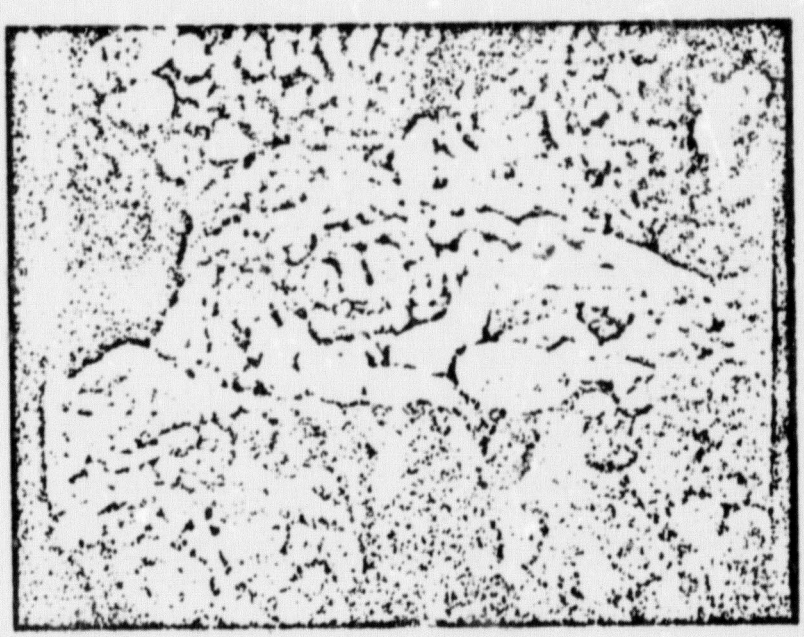
PX-14

PX 14

EXOTEC 200 X



EXOTEC 1000X



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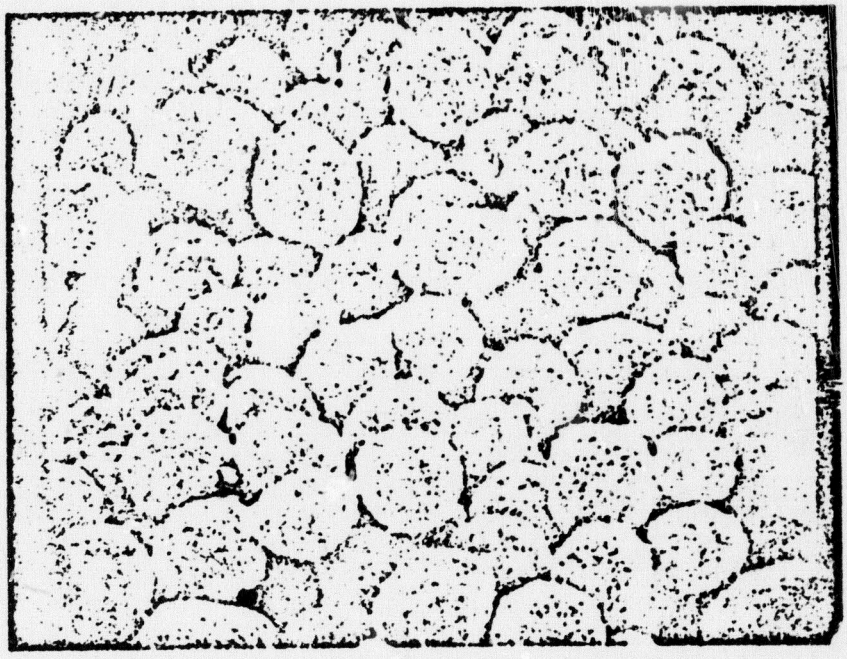
METCO 404 200X

METCO 404 1000X

E 913

14a

METCO 450 200 X



METCO 450 1000 X

November 9, 1973

PX-15

E 914

"Investigation of Exothermic Reaction of the Exotec 29904"

Prepared By:

Mahesh S. Patel
Materials Engineer
Eutectic+Castolin Institute
Flushing, New York

E 915

I. Introduction:

Exotec 29904 powder when sprayed with the use of the RotoTec torch produces an adhesive bond layer which makes it feasible for a number of metallic or alloy powders to be sprayed.

Mr. B. Brachfeld analyzed the sprayed coating of the 29904 coating to determine what phases or oxides are formed in the coatings. X-ray diffraction analysis indicated that the end product - sprayed coating, contains only Ni, NiO and aluminum oxides. The report also indicated no formation of intermetallic phases of Ni and Al. A sprayed 29904 coating was submitted to Ernest F. Fullam Inc. of Schenectady, N.Y. - an independent commercial laboratory for investigation of the coating for microprobe analysis which included investigation by X-ray diffraction, energy dispersive analysis and electron microprobe analysis. Their investigation of the 29904 coating showed that the sprayed coating contains only nickel as an elemental phase and γ-Al_2O_3.

It is theorized that Al (99% pure) reacts with O_2 and forms Al_2O_3 which is an exothermic reaction itself. This reaction generates a large amount of heat. The heat formation of Al_2O_3 is -380 kilocalories/gm mole (reference: Chemical Process Principles by Hongen and Watson; Page 253).

Visualized that these microparticles (5-7μ) of Al burning violently and generating a large amount of heat around the Ni nucleus superheats Ni particle. This superheated, or molten or partially molten particle microwelds with the relatively cold (300°-400°F.) steel, or any other metallic (except copper base surface) surface.

It is also widely known in the industry that Al has the highest chemical affinity to oxygen. A widespread use of Al results from its great chemical affinity for oxygen, whereby most metallic oxides are reduced by Al, freeing metal. Of equal value is the high temperature produced from the large amount of heat that is generated by the aluminothermic reactions (Reference: Aluminum - Vol II, Design and Application, Chapter 25 - Page 643 by Kent R. Van Horn, ASM, Metals Park, Ohio).

II. Nature of Exotec 29904 Particle:

The microscopic investigation of several representative particles showed that Al particles are not in physical contact with Ni particles. Al particles are away due to the dry resin layer around the Ni particles. It is estimated that the resin

layer, which separates the Ni and Al particles, is 1 μ to 2 μ thick, It was also found that Al particles are suspended, or held by the binder close to the Ni particles. All Al particles are coated with resin binder which actually separates each particle.

See Appendix I which includes the photomicrographs of the 29904 particles at high magnification and detailed interim report of November 7th, 1973.

Eutectic recommends a 6"-8" spray distance for 29904 powder with the use of the RotoTec torch. According to Dr. Knotek et al, reports 1-2 microseconds as the residence time for the particles. (Reference: Reactive Kinetic observations for spraying with Ni-Al powder by Knotek, Lugscheider and Eshnauer, Paper 21, Page 72, 1973 International Conference).

The following changes take place in the particles in 1-2 m sec.

1. All 2% solid resin has to burn up into smoke. Since resin burns first 400°-500°F. it retards any contact between Al and Ni.

2. Besides the 2% solid resin, all 5% Al has to react. It has to be assumed that Al cannot diffuse into Ni to form NiAl in such a short time of dwelling even if the Al comes in contact with Ni. It further can be assumed that not all Al reacts completely. This is established by the fact that the bond strength of 6" sprayed coating is lower than the 8" sprayed coating.

III. Investigation of the 29904 Particles Under Controlled Atmosphere

This investigation was conducted with the help of Frank Balistrieri in a small inductotherm crucible where atmosphere can be controlled with reasonable accuracy. 10 gms of 29904 powder - Lot 702 were placed in the crucible and the experiment was conducted under Argon, 2% oxygen-98% Argon gas and in an ambient atmosphere.

Results:

1. There was no exothermic reaction under Argon atmosphere.

2. There was some exothermic reaction under ambient atmosphere. This was witnessed as a violent reaction - started changing hot orange color to white colored powder. This reaction lasted for a few seconds.

3. There was even more exothermic reaction under 2% O_2 98% Ar atmosphere. The reaction lasted for a few seconds.

The second experiment was conducted using non-transferred plasmadyne plasma gun. The 29904 powder was injected into the arc under Argon atmosphere. See Appendix II for detailed report.

IV. Experiments with Prereacted Nickel Aluminide Powder

A. Flame structure evaluation of PP-66 and Al agglomerated PP-66 powders.

It is theorized that as previously stated in the report, Al reacts and in turn superheats the inner particle, say nickel. It was thought that this way, if the theory is correct the prereacted 5 Al 95 Ni (PP-66 manufactured by AVCO) can be made a self-bonding material. R&D Lot 165-C was obtained which contained agglomerated 5% free aluminum. See Appendix III.

Nickel powder which is being used in the 29904 powder was injected into the flame. Similarly, PP-66 powder was injected into the flame. Pictures were taken by Charles Harms of the Communication Dept. at same exposures, of the flame when Nickel (99%), powder P-66 powder, 29904 powder and Lot 165-C were injected into the flame. See Appendix III.

Observations:

1. The flame, with PP-66 powder was coldest as compared to the flame with nickel, 29904 and Lot 165-C powders. It clearly indicated that there was no reaction going on in the powder.

2. The flame with Ni powder was somewhat brighter than PP-66 flame. It is thought that pure nickel particles have more heat capacity than PP-66 particles or fine sized nickel particles oxidizing generating some heat of its own. Ni particles are not atomized (as contrary to PP-66

particles) particles and the surface is uneven (not smooth) as contrary to PP-66 particles.

It is thought that due to this observation that Ni particles which are being used in the 29904 powder, will have substantially more bonded particles or substantially more bond strength than PP-66 powder.

It is also important to note that this Ni powder, due to the rough surface will facilitate more bond strength than with similar particles with smooth surface.

3. 29904 powder and Lot 165-C powder form quite a similar exothermic reacting flame. The brightness of the flames was quite similar.

4. When PP-66 and Ni powders were sprayed on a smooth steel surface, Ni powder showed somewhat more bonded particles. An attempt is made to explain this phenomena in observation No. 2.

B. Microscopic Evaluation

29904 powder sprayed through the RotoTec torch, using standard parameter and the sprayed particles were collected in a pan. Similarly, a sprayed Lot 165-C powder was collected in the pan. Both sprayed powders appeared similar - something like burnt particles. Some were light-blue colored. The sprayed powders were mounted, polished and examined under the microscope. The observations were compared to Ni and PP-66 particles respectively (compared to 29904 and Lot 165-C). See Appendix IV.

Observations:

1. Ni particles and PP-66 particles show different metallurgical structure, as expected.

2. All aluminum and binder around Ni (29904) and PP-66 (Lot 165-C) particles are gone leaving metallic particles.

3. Sprayed 29904 particles did not show any phases similar to PP-66 particles. The particles showed to be heat effected on the outer skin though not completely covered.

E 919

4. The sprayed Lot 165-C particles appeared to be heat effected γ-Ni particles.

C. Chemical Analysis

The sprayed coatings were submitted to J. Shaulys for determination of Al content in 29904 and Lot 165-C coatings.

Results:

	Sprayed 29904	Sprayed Lot 165-C
Al	.42	.96

These results indicate that all aluminum surrounding Ni (29904) particles were oxidized away. Similar results were found with Lot 165-C powder.

D. Bond Strength

Three bond assemblies from 29904 powder were prepared and similarly three bond assemblies were made for Lot 165-C powder. These assemblies were prepared by John Nucci. The bond specimens were tested by N.Y. Testing Labs.

Test Results - (Average of Three Tests)

	Lot 702 (29904)	Lot 165-C
Bond Strength	3000 psi	3050 psi

Conclusions:

1. After observing these findings, it is concluded that when an agglomerated powder, consisting of fine sized Al and coarse sized prereacted nickel aluminide (PP-66), is injected in the oxy-acetylene flame through a torch, fine sized Al reacts exothermically, generating large amounts of heat which superheats adjacent nickel aluminide particles. These superheated, or plastisized nickel aluminide particles fuse with the steel surface.

V. Investigation of Spray Distance as Compared to Aluminum Oxide Formation in 29904 Powder

29904 powder Lot 547 was chosen to experiment this investigation. The powder was sprayed at 4", 5", 6", 7", 8', 9" and 10" from the work piece. These samples were collected and submitted to

B. Brachfeld to determine the formation of Al_2O_3 and NiO at different spray distances. A graph was plotted for Al_2O_3/NiO vs spray distance. For detailed evaluation please refer to Appendix V.

VI. Experiments on Ni-Base Alloy Powder and Coarse Sized Aluminum Powder

1. Fine sized Al was agglomerated with Ni Cr B Si (70% Ni) powder. When this powder was sprayed with the use of a RotoTec torch, the Ni Cr B Si particles were found to be bonded on the 1020 steel strip. The percent of bonded particles was estimated to be 80-90%.

2. A coarse sized aluminum powder (-170 +325 mesh sized particles) was sprayed through the RotoTec torch. It was found that aluminum particles were found to be bonded on the 1020 steel strip. The percent of bonded particles was estimated to be 70-80%. An experimental lot was obtained wherein fine sized Al powder was agglomerated with the coarse sized Al powder. When this powder was sprayed using a RotoTec torch, the bonded particles were found to be 100% on the 1020 strip.

VII. Conclusions:

1. The only exothermic reaction in the Exotec 29904 powder is the reaction of Al to Al_2O_3 and some Ni to NiO.

2. Al reacts exothermically and generates large amounts of heat.

3. Out of all the possible reactions, the heat formation of Al_2O_3 has the most negative values of any of the heat formation reactions.

4. The many fine sized Al particles around each Ni particle generate large amounts of heat during reaction which in turn superheats the Ni particle. This superheated or plastisized Ni particle microweld, or fuse on the work piece.

5. It is established that most Ni base alloy powder can be made self-bonding material by agglomerating with fine sized Al powder.

6. There is no intermetallic phase formed in the sprayed 29904 powder.

7. Al spherical particles are separated from the Ni particle by the thickness of the solid resin. That is, a thin layer of resin surrounds each Ni particle.

E 922

November 7, 1973

Mr. J. F. Quasa

Mr. M. Patel

29904 POWDER PARTICLE EVALUATION

We mounted and polished several particles from two different lots of Exotec 29904 powder. Lot 547 was a considerably old lot but Lot 694 was a recently manufactured lot. Many particles were examined under the microscope at high magnification.

The following observations were made:

1. The nickel particles were substantially larger when compared to the aluminum particles. Aluminum particle size is ranged from 5-7μ while the nickel particle size average is 70μ.

2. Aluminum particles and nickel particles, generally speaking, are spherical in shape.

3. Substantial number of Exotec particles were not completely covered by aluminum particles.

4. Each aluminum particle is found to be held by resin. In other words, each aluminum particle is coated with resin and they are situated next to each other but without any physical contact between each other. This is contrary to general opinion because it is thought that aluminum particles touch each other and form a continuous layer around the nickel particles.

5. We found that there were a fraction of a percent of aluminum particles in contact with the nickel particles. The majority of aluminum particles are away from the nickel particles. We found that the nickel particles are coated with resin which forms a thin layer around the nickel particles and aluminum particles are glued on the resin layer. It seems that the resin layer is continuous around the nickel particles without being broken up by aluminum particles.

Please find attached, five photomicrographs of Exotec 29904 particles taken at 1200X and at 500X. The 500X pictures were taken in one lab and M1200X pictures were taken by an outside commercial laboratory.

Mr. J. F. Quaas November 7, 1973

NOTE: The gap showing between aluminum and nickel is due to resin which does not show distinctively in the picture due to the nature of microscopy.

MP:hpc
att.

E 924

Eutectic+Castolin Institute
40-40 172nd Street
Flushing, New York 11358

November 7, 1973

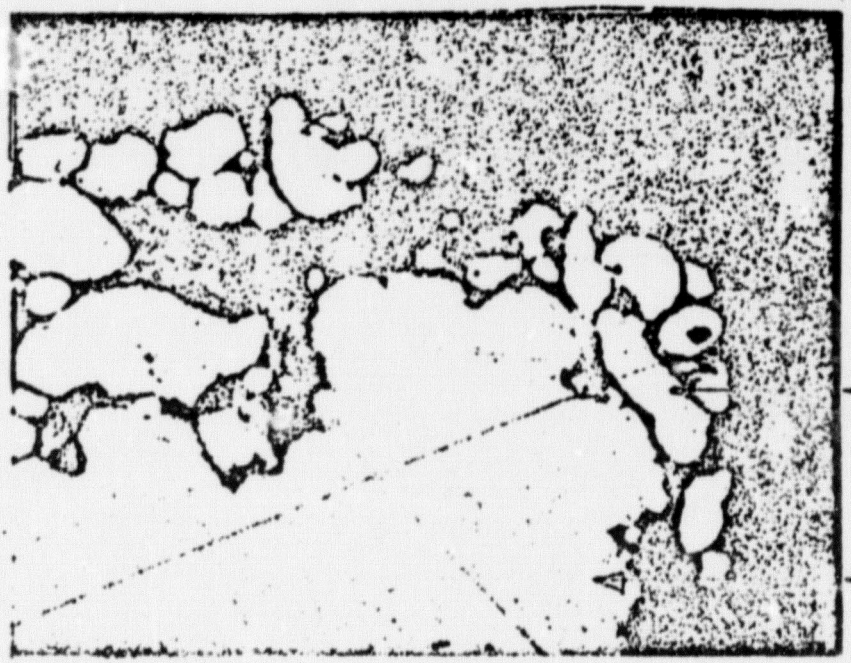
Powder: Exotec 29904
Lot : 547 M. No. 2563
Etchant: None
Magnification: 1200X

E 925

Eutectic+Castolin Institute
40-40 172nd Street
Flushing, New York 11358

November 7, 1973

Powder: Exotec 29904
Lot : 694 M. No. 2560
Etchant: None
Magnification: 1200X



E 926

Eutectic+Castolin Institute
40-40 172nd Street
Flushing, New York 11358

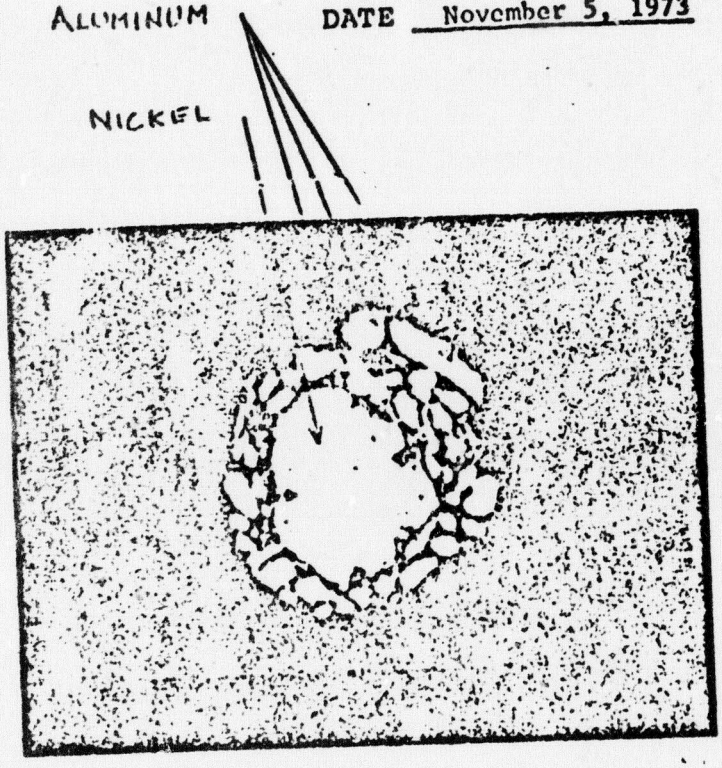
November 7, 1973

Powder: Exotec 29904
Lot : 694 M. No. 2560
Etchant: None
Magnification: 1200X

E 927

EUTECTIC CORPORATION

PHOTOMICROGRAPH RECORD
DATE November 5, 1973



Specimen # 2463

Magnification 500X

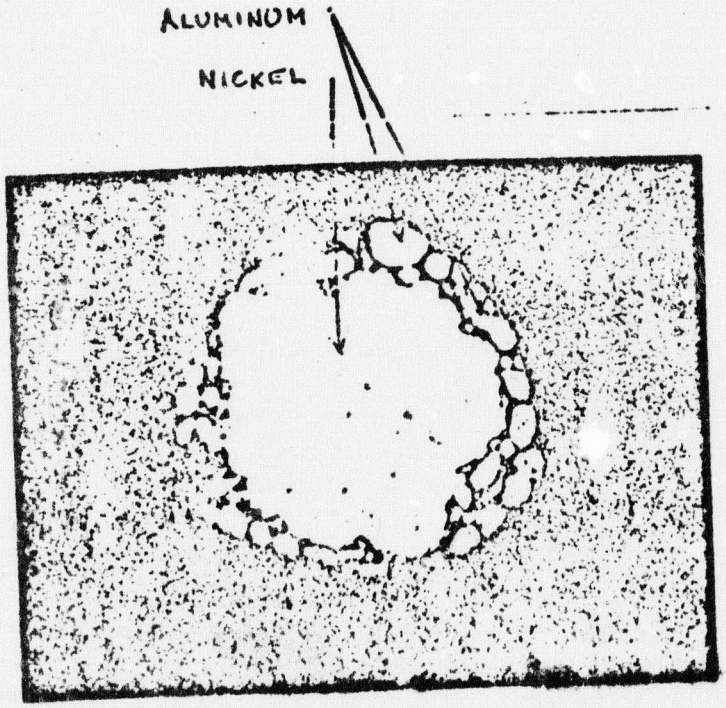
Etchant None

Project

Process Cross Section

Sample Description

Exotec 29904 Lot 547



Specimen # 2463

Magnification 500X

Etchant None

Project

Process Cross Section

Sample Description

Exotec 29904 Lot 547

E 929

Internal Correspondence
Flushing

Eutectic + Castolin Institute
for the Advancement of Maintenance
and Repair Welding Techniques
PERMANENT TECHNICAL ASSISTANCE

Exclusive Processes • Wearfacing Alloys • EutecRod Alloys • EutecTrode Alloys
Continuous Electrodes • Powdered Alloys • Chemical Aids and Fluxes

Date November 2, 1973
To Mr. J. F. Quaas
From Mr. M. Patel
Copies

Subject
EXPERIMENTS ON 29904 POWDER

As per your instructions, the plasma (non-transferred Plasmadyne gun) was ignited using argon gas at 200 amps and 80 volts. The argon gas flow was kept at 55-60 psi. It is believed that no oxygen is introduced into the plasma flame as argon gas pressure was kept high. The 29904 powder, Lot 702 was injected into the flame which is outside of the nozzle.

As we know, exothermic reaction brightens up the flame and creates a high glaring which is quite visible through the dark shielding glass. I could not see any of these reactions occurring within the particles.

Since I could not see any reaction occurring, I looked for other reactions. I used light colored glass and while protecting my eyes, I tried to determine whether a light colored flame occurred due to the injection of the powder. The only observation I made was a light blue, very minor flame. This blue flame might have come from vaporization of the aluminum powder which is the outside part of 29904 particle.

COMMENTS:

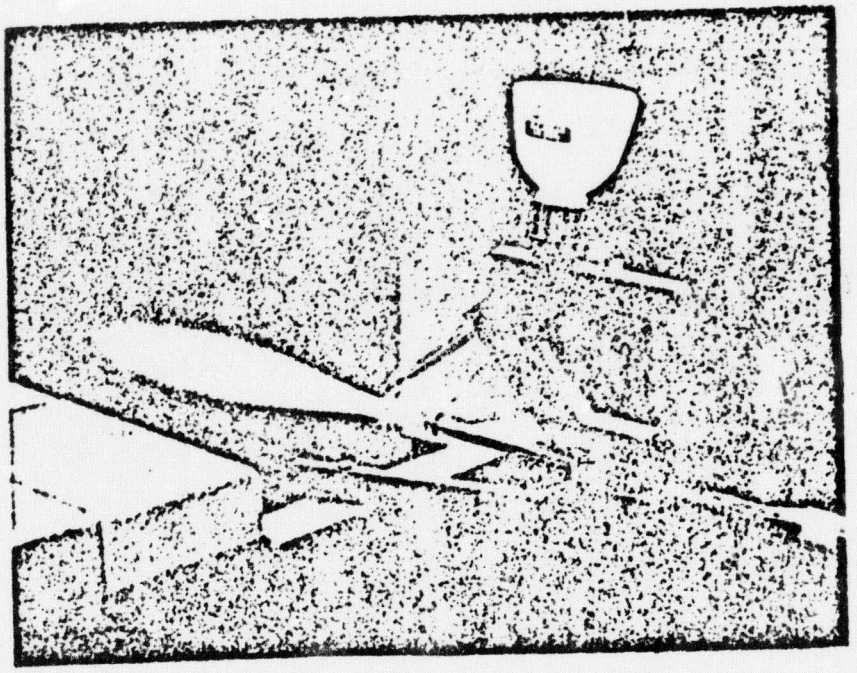
It can safely be concluded that in order for an exothermic reaction to occur in the 29904 powder, oxygen is required. It can be easily understood that 29904 particles are coated with fine sized aluminum and this aluminum touches the oxy-acetylene flame first. It can further be understood that aluminum can react with oxygen forming an exothermic reaction which generates a large amount of heat. The heat formation of Al_2O_3 is -380 kilocalories per gram mole. (Reference: Chemical Process Principles by Hougen and Watson - Page 253).

MP:hpc

E 930

EUTECTIC+CASTOLIN INSTITUTE
40-40 172nd Street
Flushing, N. Y. 11358

Nov. 7, 1973

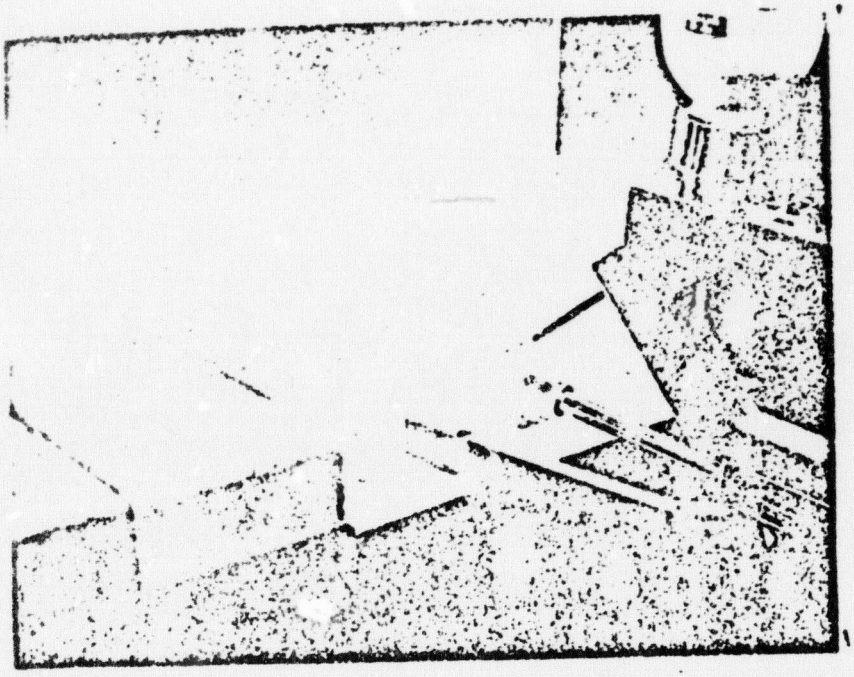


The RotoTec flame with standard parameters, without spraying any powder.

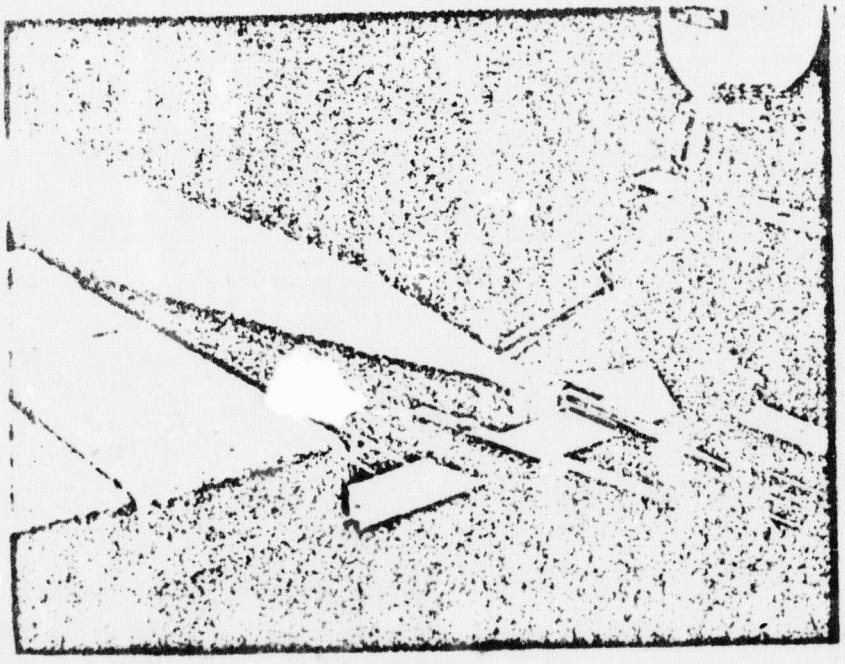
E 931

EUTECTIC+CASTOLIN INSTITUTE
40-40 172nd Street
Flushing, N. Y. 11358

Nov. 7, 1973



Lot 165C in the process of being sprayed, showing an increased brightness of the flame due to the exothermic reactions of the particles.

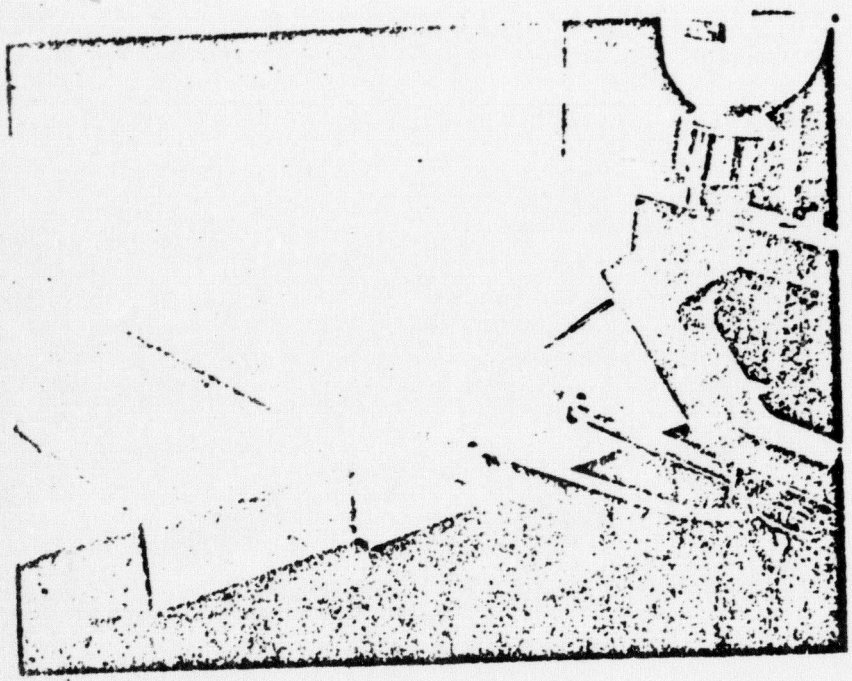


PP-66 in the process of being sprayed. It can be seen that there is no exothermic reaction in the particles.

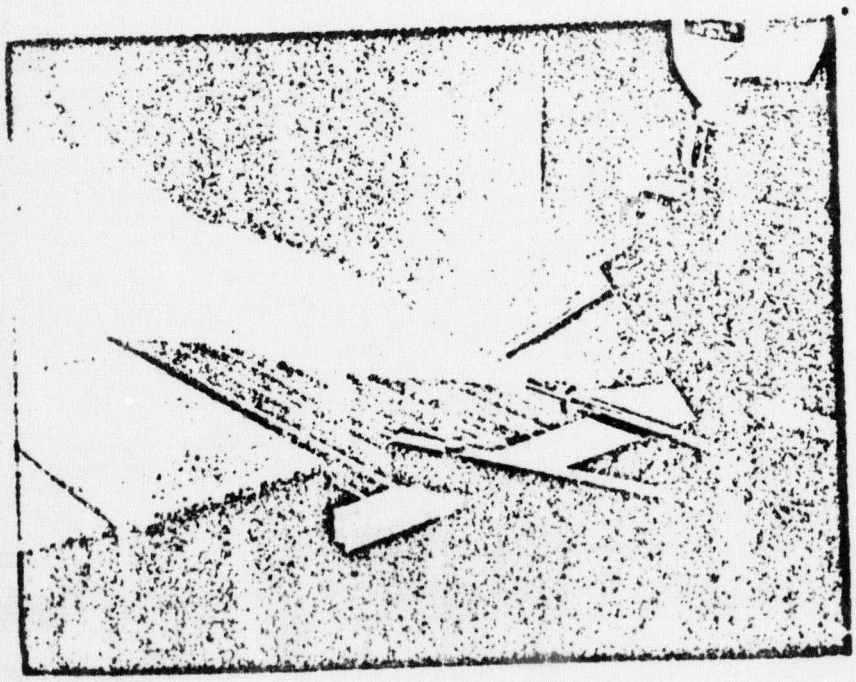
E 932

Eutectic+Castolin Institute
40-40 172nd Street
Flushing, N. Y. 11358

Nov. 7, 1973



Exotec 29904 in the process of being sprayed showing an increased brightness of the flame due to the exothermic reactions of the particles.



Nickel (99%) in the process of being sprayed showing very little exothermic reactions. This flame is somewhat brighter than PP 66 flame.

E 933

November 2, 1973

Mr. J. F. Quass

Mr. M. Patel

PREREACTED NiAl - EXPERIMENT

This report is a continuation of my 10/31/73 memo.

As per your suggestion, the following experiments were conducted. The powder was prepared by John Nucci of R&D and the experiments were carried out by S. Tilkaren of the Quality Control Dept.

PP-66 (5 Al 95 Ni - CNi) Powder

1. P-66 powder was sprayed through the RotoTec torch using standard parameters. It was observed that no exothermic reaction occurred when these particles were injected into the flame. The oxy-acetylene flame brightens up when there is an exothermic reaction and this did not happen when this powder was used. The powder was sprayed on a clean, oxide-free and smooth 1/8" thick x 1" wide x 5" long 1020 steel plate at a 6" spray distance. The sprayed coating thickness was 0.006" - .008" thick. Then high shrinkage 308 S.S. wire was sprayed on the coating as an overcoat. Since the P-66 coating has very poor bond strength, the overcoat wire coating peeled when it formed a thin coating. The thickness of the peeled coating was measured. The bonded particles were observed on the 1020 steel strip.

2. Exotec 29904 powder, Lot #702 was obtained from Quality Control. The aluminum content of the lot is 5.1% Al. This powder was sprayed on a similar 1020 steel strip as described above at a 6" spray distance. Similarly, as described above, the coating was coated with 308 S.S. wire, which peeled off as it became thick. The thickness of the peeled coating was measured. The bonded particles were observed on the 1020 steel plate.

3. Fine sized aluminum was agglomerated with P-66 powder. The chemical analysis indicated that 5.6% aluminum was glued on the P-66 particles. So, another lot identified as Lot 165 C of the powder was made to adjust the chemistry arriving at approximately 5.0% aluminum glued with the P-66 particles. Similarly, as described above, a 0.006-0.008" thick coating was obtained on the 1020 steel strip from the Lot 165 C. Again, as described above, the coating was peeled off. The thickness of the peeled coating was measured. The bonded particles were observed on the 1020 steel strip.

Mr. J. F. Quasa

November 2, 1973

Results of the three experiments:

COATING	THICKNESS OF PEELED COATING	BONDED PARTICLES
P-66	0.025 - 0.030"	5%
29904 Lot 702	0.10 - 0.12"	85%
5% Al (95% P-66)	0.10 - 0.13"	80%

NOTE: Quality Control Dept. accepts a powder (Exotec 29904) as a good bonding material when it obtains 75% bonded particles on 1020 steel strip as described in experiment #1.

CONCLUSION:

1. P-66 powder which is prereacted 5 Al 95 Ni powder is not a bonding material when used with the RotoTec torch. There is no exothermic reaction occurring in the particles when injected in the RotoTec flame.

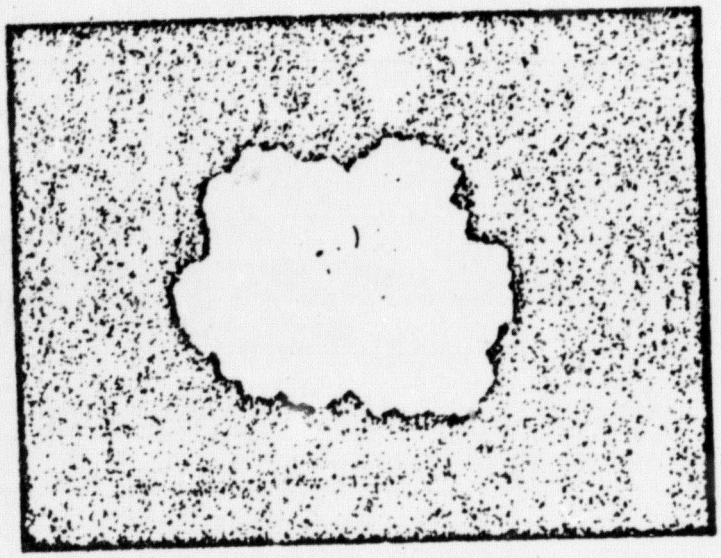
2. P-66 powder can be made a good bonding material like 29904 powder when it is agglomerated with approximately 5% fine sized aluminum. There occurs an exothermic reaction in the RotoTec flame when aluminum clad on P-66 particles is injected in the RotoTec flame. This exothermic reaction and brightening up of the flame is very similar to the reaction and brightening up being produced during the 29904 particles being injected in the RotoTec flame.

MP:hpc

E 936

EUTECTIC CORPORATION

PHOTOMICROGRAPH RECORD
DATE Nov. 7, 1973



Specimen # 2571

Magnification 750 X

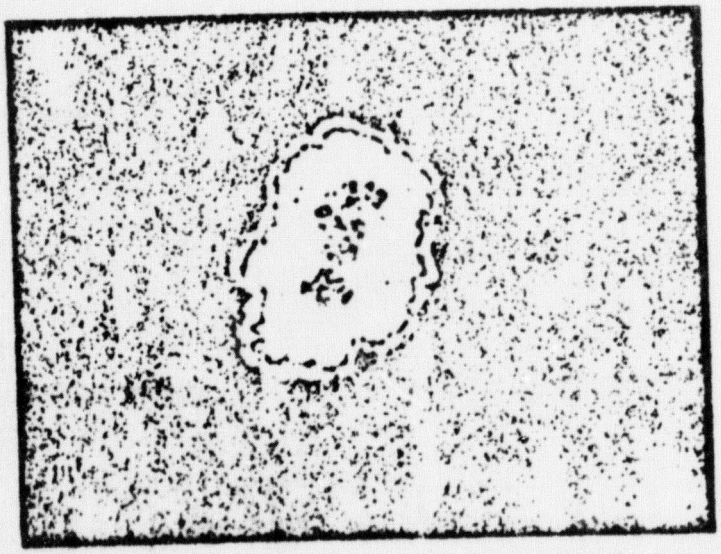
Etchant None

Project

Process Cross Section

Sample Description

Ni



Specimen # 2571

Magnification 750 X

Etchant Carapella's Reag.

Project

Process Cross Section

Sample Description

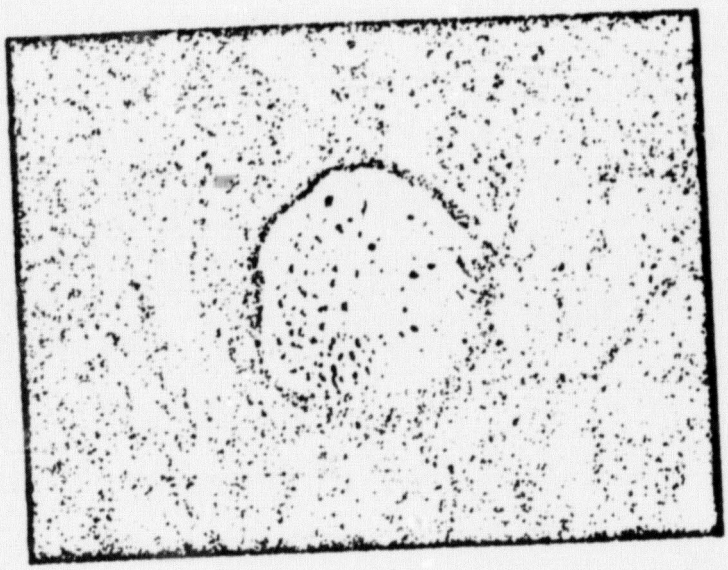
Ni

Form No.

E 937

EUTECTIC CORPORATION

PHOTOMICROGRAPH RECORD
DATE Nov. 7, 1973



Specimen # 2567

Magnification 750 X

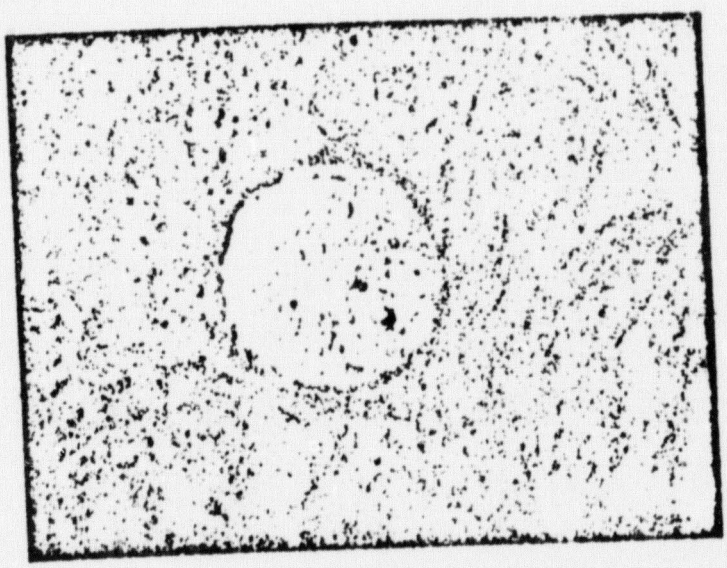
Etchant None

Project

Process Cross Section

Sample Description

Sprayed 2990 Lot 702



Specimen # 2567

Magnification 750 X

Etchant Carapella's Reag

Project

Process Cross Section

Sample Description

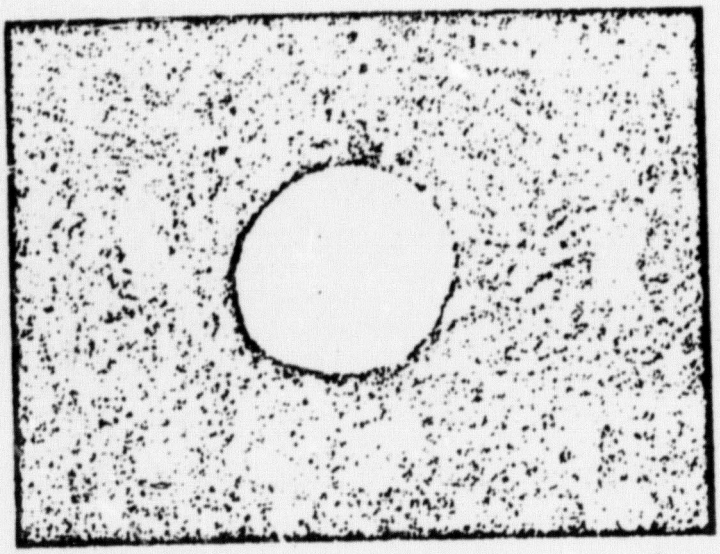
Sprayed 2990 Lot 702

Form

E 938

EUTECTIC CORPORATION

PHOTOMICROGRAPH RECORD
DATE Nov. 7, 1973



Specimen # 2570

Magnification 750 X

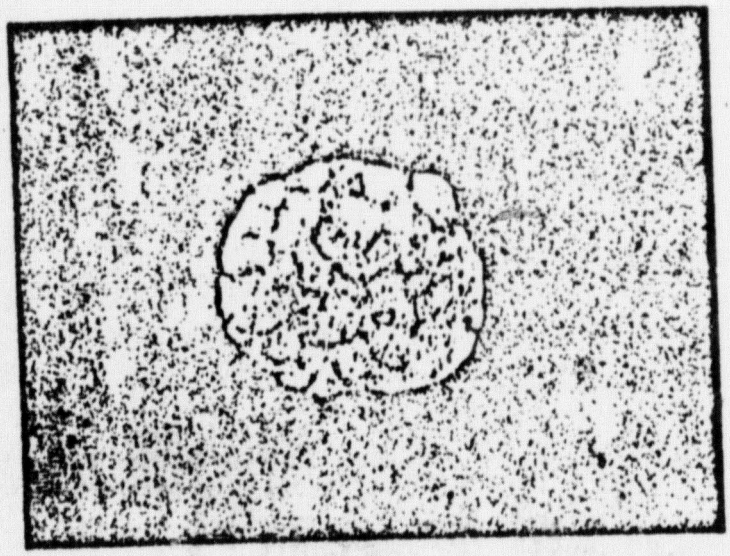
Etchant None

Project

Process Cross Section

Sample Description

PP-66 Prereacted
5 A195Ni



Specimen # 2570

Magnification 750 X

Etchant Carapella's Reag.

Project

Process Cross Section

Sample Description

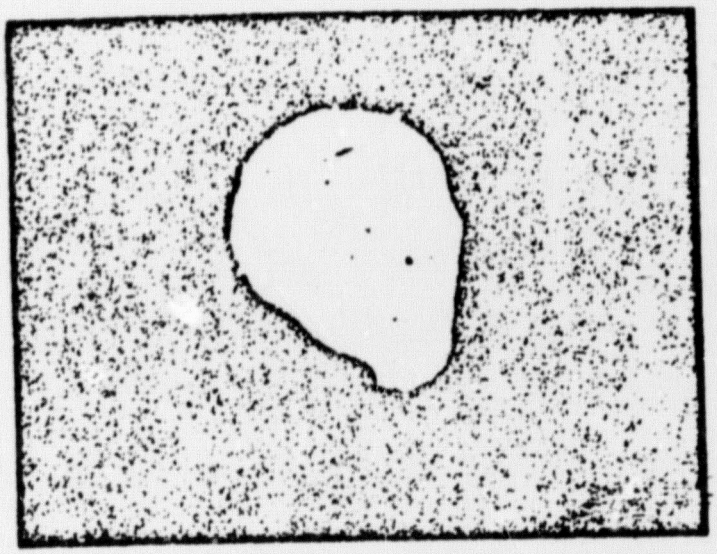
PP-66 Prereacted
5A195Ni

Form No.

E 939

EUTECTIC CORPORATION

PHOTOMICROGRAPH RECORD
DATE Nov. 7, 1973



Specimen # 2566

Magnification 750 X

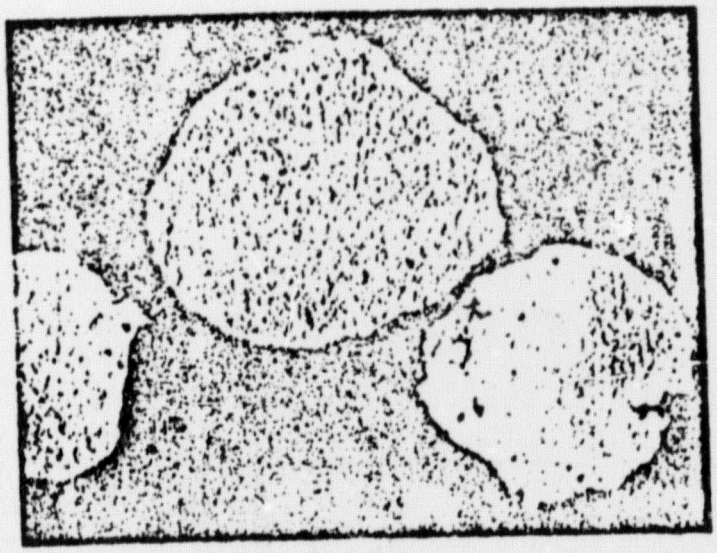
Etchant None

Project

Process Cross Section

Sample Description

Sprayed Lot 165 C



Specimen # 2566

Magnification 750 X

Etchant Carapella's Reag.

Project

Process Cross Section

Sample Description

Sprayed Lot 165 C

Form No

E 941

Internal Correspondence
Flushing

Eutectic + Castolin Institute
for the Advancement of Maintenance
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Continuous Electrodes • Powdered Alloys • Chemical Aids and Fluxes

Date November 7, 1973
To Mr. M. Patel
From Mr. B. Brachfeld/BB
Copies Mr. J. F. Quaas

Subject
EXPERIMENTAL EVIDENCE FOR THE PROPOSED Al_2O_3 THEORY OF Ni/Al POWDER BONDING (29904)

INTRODUCTION

As is well known, the original theory behind the Ni/Al bonding mechanism was that, in the flame spray, Al combines with Ni to form the intermetallic NiAl. In so doing heat is released which helps soften the powder particles and thus enhances bonding onto the sprayed piece. As previously reported (8/14/70), X-ray diffraction analysis repulsed this theory in that no evidence of NiAl type compounds could be found in the sprayed powder. However, oxides of Ni and Al were detected. Using this experimental evidence, a new theory was proposed by M. Patel which stated that the most important reaction occurring in the flame spray was that of Al being oxidized to Al_2O_3. In so doing, it releases heat which helps the powder bonding - no NiAl intermetallic compounds needed to be formed.

EXPERIMENT

To substantiate this new theory, samples of sprayed NiAl powder (29904) were collected by M. Patel in which the spray distance varied from 4 to 10 inches. X-ray diffraction analysis showed that all the sprayed samples contained only Ni, NiO and Al_2O_3. Next, the X-ray intensity ratio of Al_2O_3 to NiO was plotted vs spray distance. Looking at the attached graph, it is immediately seen that the intensity ratio is a maximum at 7 inches - exactly the distance at which the optimum spray results are obtained.

What is happening is that as the spray distance is increased from 4 inches, the amount of Al_2O_3 formed is increasing in relation to the NiO also being formed. After reaching a maximum at 7 inches, the ratio decreases because all of the free Al has reacted to Al_2O_3 while the Ni, being present in a far greater amount, is still being converted to NiO.

CONCLUSIONS

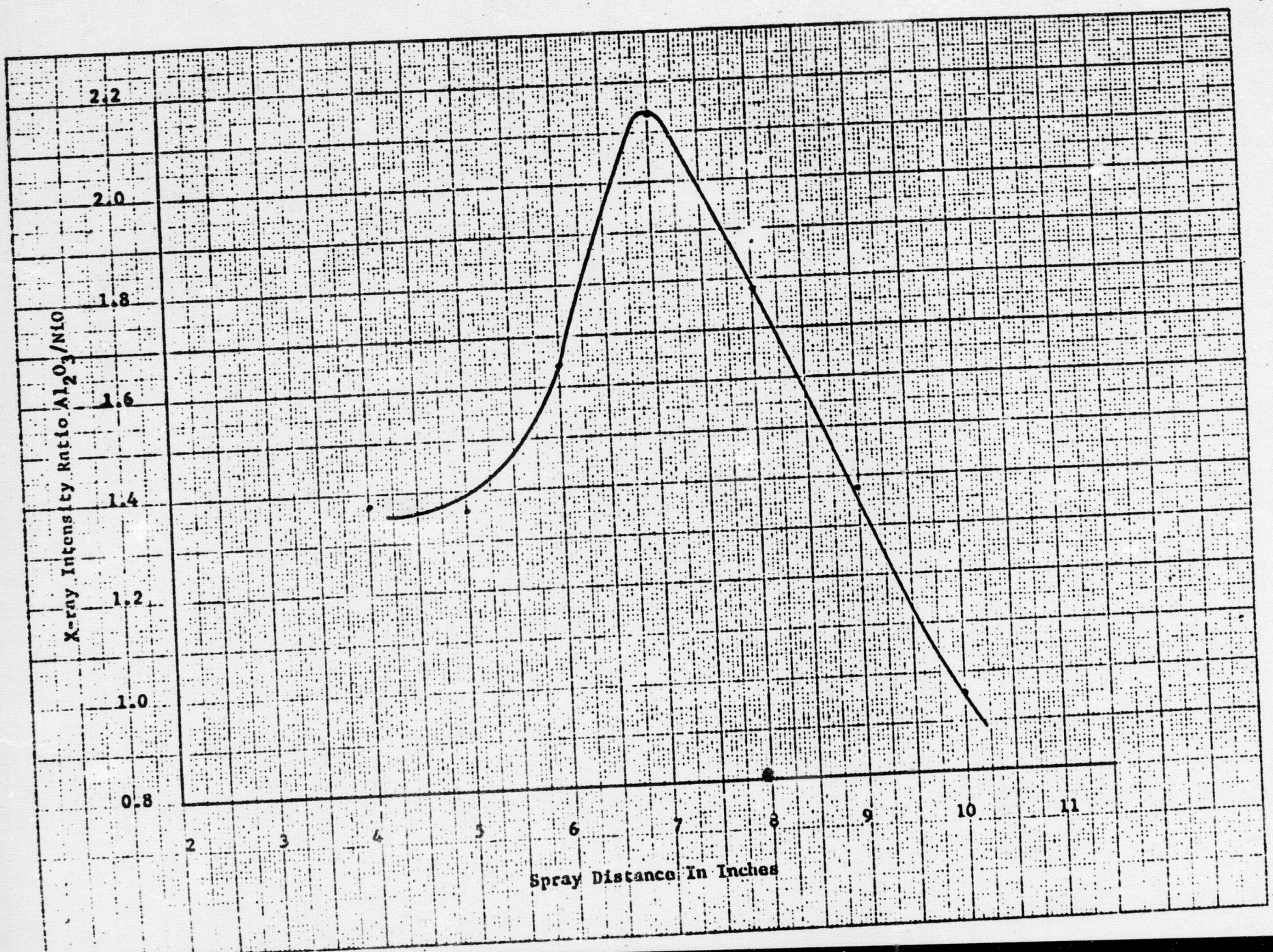
1. The bonding mechanism of Ni/Al powder does not depend on the formation of NiAl type intermetallic compounds.

2. The Al_2O_3/NiO X-ray intensity ratio, peaking at 7", is experimental proof that the formation of Al_2O_3 from free Al is one of the prime prerequisites for good bonding of Ni/Al powder.

3. The bonding efficiency increases with increasing spray distance only as long as there is free Al to be converted to Al_2O_3.

hpc

RETURNED 1.8.6.4.4


X-ray Intensity Ratio Al_2O_3/NiO
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
2
3
4
5
6
7
8
9
10
11
Spray Distance In Inches

E 942

Combination (Exothermic) Reactions Upon Heating

Layered Coatings of Various Metals

October 6, 1955

ST I and Al - Exothermic reaction progresses throughout entire piece if preheated and then ignited at one spot.

NICHROME (METCOLOY 33) and Al

1 - A coating stripped from base, preheated and ignited at one spot will react as (ST #1 and Al) except that preheat must be higher, and the progress of the reaction through the piece is slower.

2 - On 1/8" t steel backing. Quick, local, overheating will cause the corbination reaction in the spot overheated only. The reaction will not progress through the rest of the coating.

On 1/8" t steel backing. Preheating to approx. 1200-1300° F. and then localizing heat in one spot triggered the reaction in the overheated spot only - the reaction did not progress through the rest of the coating. As the torch was moved, the heated portion under the flame reacted until the entire panel would no longer show any reaction. I suppose that, if the entire panel were preheated hot enough, the reaction could progress through the entire coating if triggered by local overheat.

Cr and Al

(Hardy CR - 160 as sprayed on Combustion Eng'g Tubes).

While the exothermic combination reaction apparently occurred upon heat treating the Comb. Eng. furnace tubes, no reaction could be obtained here at the Lab. Stripped coatings and coatings adhering to a steel base were heated without any reaction or volume change occurring. Small quantities of Cr and Al powders, mixed, showed some signs of the combination reaction.

Ni and Al

If heated slowly (comparatively) the ni-al sandwich will not ignite and, having once been brought up to 1200° - 1400° F, no further heating to any temperature up to MP will cause any reaction.

Rapid local overheating of one corner of a ni-al sandwich will trigger a fairly violent exothermic reaction with the resultent alloying of the Ni and Al. The entire mass of the sheet will coalesce into pools of the alloy formed.

F. J. Dittrich

FJD/k

Epothemic Pat Appl

Ti - Ni
Al - Palladium
3 Prim art
Ti Ni
Pd
Ti Ni
Pd
Pd
Pd
Pd
10
Pd
Pd
W/
P7
Ni P ex
delete

P10 "Resin wires does not depend upon colour of ... Vision" ?

P13 Rest ... - ... 20% ...

PX-22

Maybe shall add

~~All P~~

Ni Zr

~~P Co, Cr, Fe~~

Co Si

Mo Si

~~Cr P~~

Ni Si

Si Ta

Maybe should delete

~~Cr P~~ (Jim)

Cs Ng (Hg not parallel)

Ng N (N " ")

Hg K etc (Hg " ")

H Zn

Ni Ta (Jim)

~~Chromium~~ (?) with 3 P

" " " with 1 P

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(5824)